"The performance of rotary concentric cylinder fractionating columns"

by

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Chapter I

1.1. Aim of work

This work is a continuation of a project started by Matterson (1) and Shahbenderian (3), the aim of which is to elucidate the mechanism of operation of concentric cylinder wetted wall fractionating columns with the inner cylinder stationary or rotating. In this chapter are given the reasons for the choice of this type of column for this investigation and the aims of the present research programme.

1.2. Prediction of performance

In any distillation column, if the physical situation is known and the liquid and vapour phases behave in a predictable and determinate fashion, it should be possible to predict the column performance (i.e. the separating power for given operating conditions) from the appropriate laws or correlations governing rates of convective mass transfer. One of the aims of the present work is to examine the validity of accepted methods for making such predictions by comparing the experimental data from a particular type of column with the theoretically predicted values.

1.3. Choice of suitable distillation column

There are many types of fractionating column in common use. These fall into three principal classes; plate columns, packed columns and wetted-wall columns. Only/

Only this last-named class contains columns in which the vapour and liquid phases behave in a predictable and determinate manner. The fluid mechanical situation in plate columns of various types is usually extremely complex, while the flow paths in packed columns are neither reproducible nor predictable.

1.31 Open tube column

The simplest wetted wall column is the open-tube column. The vapour ascends the main body of the tube, is condensed, and the reflux descends on the tube inner surface, spread in a uniform film.

In 1942, Westhaver (6) and Kuhn (7) independently derived a theoretical expression for H.E.T.P. in an open-tube column for the case of laminar vapour flow. When the mass transfer resistance is exclusively on the vapour side, this expression is:

$$H = \frac{11}{48} \frac{u_v r^2}{D_v} = 0.023 \frac{u_v r^2}{D_v}$$

They considered the mass transfer processes accompanying distillation to be analogous to the heat transfer process in the corresponding heat exchange situation with constant heat flux at the wall.

Later, in 1955, Malyusov (8) developed a similar expression:

$$H = 0.017 \frac{u_v r^2}{D_v}$$

in which he assumed constant temperature at the wall instead of constant heat flux in the heat transfer analogue.

There/

There is good reason to suppose that the assumption of constant wall flux made by Westhaver and Kuhn is correct.

It is difficult to provide positive experimental verification of either one or other of these relations since the performance of the open-tube column is very poor except at low throughputs. It is therefore not possible to alter the independent variable over a wide range to obtain a suitably broad range of accurately measurable values of separating power so as to establish the form of the relation. In addition, the physical constants of many suitable test mixtures are uncertain, so it is difficult to verify the value of the constant in the theoretical equations.

1.32 Concentric tube column

The concentric-tube fractionating column is another such column amenable to theoretical treatment. For given column diameter and throughput, better separating power can be obtained than with an open tube; and the vapour velocity can be altered independently of the throughput by varying the annular gap width. The performance can thus be checked against theoretical prediction over a wider range of operating conditions. However, an uncertainty not present in the open tube column is inherent in this column: because there are two solid surfaces instead of one, reflux may descend one, or both, walls.

For one wall evenly wetted, Westhaver predicted:

$$H = \frac{52}{140} \frac{u_v b^2}{D_v}$$

and for both walls evenly wetted, with the reflux equally divided between each wall:

H/

$$H = \frac{17}{140} \quad \frac{u_v b^2}{D_v}$$

For identical boilup rates, the separating power is thus approximately three times greater for the latter case than for the former. Flower (22) has shown that for reflux unequally divided between the walls:

$$H = H_{II} \left(1 + \frac{140}{17} \delta^2\right)$$

where H_{II} is the H.E.T.P. for both walls equally wetted with reflux, and the reflux is divided between the surfaces in the proportions $(0.5 + \delta)$ and $(0.5 - \delta)$. Unless special attention is paid to the design of the column to ensure a known division of reflux, it is not possible to verify Westhaver's equation. In most of the published investigations with these columns, this point has been largely disregarded. Often, however, it is possible to infer that the results are not inconsistent with Westhaver's theory.

1.33. Rotary concentric tube column

A third type of wetted wall column is the rotary concentric cylinder fractionating column. The rotation of the inner cylinder is in most cases sufficient to throw off reflux by centrifugal action, so the problem of reflux division is avoided. Moreover, such columns are known to have very high separating power (2 , 3 , 4). This means that the effect of the independent variables can be studied over a much wider range than is possible in the open tube case. In addition, a new independent variable is introduced, namely the speed of rotation of the inner cylinder, which ought to have a predictable effect on separating power.

1+/

It is possible to infer, from the work of Kaye and Elgar (21), Flower (22) and Todd (23) what will be the motion of the vapour at a given boilup rate and rotor speed in such a column. Furthermore, if the conditions of operation are chosen such that the vapour motion is laminar + vortex, experimental correlations developed from the data of these and other workers for heat and mass transfer in similar systems indicate that the following relations would be expected:

$$N \propto (Ta)^{\frac{1}{2}} \quad \text{at constant } (Re_{ax})$$

$$H \propto (Re_{ax}) \quad \text{at constant } (Ta)$$

These two types of distillation column described in 1.32 and 1.33 are therefore suited to the investigation of the theory of distillation, since the performance can be predicted for various operating conditions, and compared with experimental data obtained over a wide range of operating variables.

1.4. Purposes of investigation

The general programme of work in this field, begun by Matterson and continued by Shahbenderian and Flower, has a twofold purpose:

a) To put the practical design of rotary concentric cylinder fractionating columns on a rational basis, so that the scope and limitations of this type of distillation equipment may be properly assessed;

b) To examine the applicability to this particular case of general theories of mass transfer and distillation.

The/

The present investigation, in which two columns of different size but similar geometry were used, has been directed to these ends. In particular, it attempts to resolve the apparent conflict between the distillation data of Willingham et al. (4) and of Shahbenderian (3), and of both these sets of data with the predictions made from other kinds of mass transfer measurements (notably those of Flower). In the former paper, under the relevant conditions of operation, $N \propto Ta$, while Shahbenderian's data shows no significant dependence of separating power on rotational speed. The mass transfer studies of Flower, Shahbenderian, Todd and others lead to the expectation that $N \propto (Ta)^{\frac{1}{2}}$.

1.5. Practical uses

Rotary concentric cylinder fractionating columns are of practical interest because of their high separating power at relatively high vapour velocities, and their low holdup and pressure drop. It is clear that such columns should be of use in the separation of small amounts of close-boiling materials on a laboratory scale.

The stationary concentric tube column is also capable of efficient separation, provided care is taken with the reflux division. It is possible that the performance with the rotor stationary would be better than that with the inner cylinder rotating at low speed. If this is so, it is of interest to determine the minimum rotational speed necessary for improvement in separating power.

CHAPTER II.

2.1. Introduction.

In this chapter, it is intended to present the outline of theories for the operation of concentric tube distillation columns with the inner cylinder:

(a) stationary

(b) rotating.

From these theories, inferences will be drawn which will then be compared with the experimental data of various workers. In appropriate cases, and where there are apparent contradictions with theory, more detailed analyses and comparisons will be presented in Chapter V along with the discussion of experimental data obtained in the present study.

2.2. Stationary-tube columns.

2.2.1. Theory.

In 1942, Westhaver (11) outlined the theory of operation of an open tube distillation column which he extended to cover the case of a concentric tube column operating either

i) with only the inner tube wetted

ii) both tube surfaces equally wetted,

with reflux:

Westhaver justified the assumption of equilibrium between the liquid surface and the vapour in its close proximity from kinetic theory considerations. The case of equilibrium reached under conditions of total reflux was considered, and assumptions of a uniformly distributed film, laminar flow of vapour equivalent to that obtained between 2 parallel plates and negligible liquid side resistance to mass/

mass transfer were made. This resulted in the derivation of the following expressions:

$$(H_v)_I = \frac{57}{140} \frac{\bar{u}_v w_v^2}{D_v} \qquad 2.1$$

for one wall wetted

$$(H_v)_{II} = \frac{17}{140} \frac{\bar{u}_v w_v^2}{D_v} \qquad 2.2$$

for both walls wetted.

Neglecting liquid side resistance, the separating power at identical boilup rates is approximately three times greater when the reflux wets both walls equally than when only one wall is wetted. It is thus most important when designing such a distillation column to ensure that the reflux is evenly distributed between both walls, or that the reflux proportions are known when comparison is made between theory and experiment. Flower (22) has shown that

$$H_v = (H_v)_{II} \left(1 + \frac{140}{17} \delta^2\right)$$

where $(H_v)_{II}$ is the HETP for both walls wetted and the reflux is divided between the two walls in the proportion $(0.5 + \delta)$ and $(0.5 - \delta)$.

In Westhaver's theoretical treatment the following further assumptions were made:

1) The test mixture is close-boiling ($\alpha < 1.1$)

2) the vapour velocity up the tube is constant

3) the vapour velocity is large compared with the liquid velocity

4)/

4) HETP is large compared with the gap-width

5) the column operation is adiabatic

6) the vapour diffusivity is constant with composition

7) Longitudinal diffusion is negligible

8) Entrance length is small compared with the column-length.

In all the experimental work considered below, the test-mixture used is either n-heptane/methylcyclohexane or 224 trimethylpentane /methylcyclohexane. Not only are the relative volatilities of these mixtures below 1.1 (which meets requirement 1), but an assessment of suitable test-mixture for evaluation of high-performance fractionating columns in Chapter III shows that both these mixtures are substantially ideal, with chemical and physical properties which do not vary appreciably with composition. Provided column operation is adiabatic, requirement 2 (and of course 5) will be met. Other assumptions will be considered when individual cases are examined.

2.2.1.1. Liquid side resistance.

Shahbenderian has shown that the HETP due to liquid side resistance is given by:

$$H_L = \frac{33}{140} \frac{\bar{u}_L w_L^2}{D_L} \qquad 2.3.$$

The total HETP is obtained by adding H_v to H_L. There is evidence that liquid side resistance is unimportant in stationary concentric tube columns. Although the absolute values of the diffusivities D_L and D_v are not known they can be estimated, and an estimate thus made of whether H_L is likely to make a significant contribution. This assumes that existing correlations for D_L and

D_v/

D_v are not very far wrong.

2.2.1.2. Analysis for wide gaps.

In his theory, Westhaver assumed that the vapour flow in an annular gap was identical with that between two parallel plates separated by a distance equal to the annular gap width. In Appendix A an expression for HETP is derived using the correct velocity profile for laminar flow in an annulus. In all cases the value of HETP derived using the expression for annular laminar flow is lower than that obtained when the curvature of the gap is neglected, as in the simple parallel plate case. These theoretical values of HETP were calculated for various columns described in the literature and are compared in Table AI in Appendix A with the corresponding parallel plate values. For the very low b/r_o = 0.071 of Shahbenderian (3) the discrepancy is 0.8% and for the highest b/r_o of Hall and Palkin (13) it rises to 9.2%.

2.2.2. Operation of stationary concentric-tube columns.

2.2.2.1. Material losses at stillhead.

It is important to ensure that the column operates at total reflux. Coulson (9) has shown that a slight leak of distilland at the stillhead can reduce the separating power of high performance columns considerably.

2.2.2.2. Heat losses.

Heat losses may occur:

i) at the stillpot

ii) along the column

iii) at the column section adjacent to the condenser.

Heat loss at the last probably will not be significant in causing the column conditions to depart from Westhaver's assumptions, as its effect will be to extend the condenser proper into the rectifying section by a small amount thereby causing material to be condensed before the distillate take-off point.

The other two sources of heat loss may be serious. In small laboratory scale columns the amount of heat required to maintain a typical boilup rate of 300 ml/hr. is very small, c. 18 watts. Unless the stillpot is very well lagged and shielded from draughts in order to eliminate heat loss fluctuations, significant variations in boilup rate may be expected.

At these low boilup rates, a small radial heat flux from the column can be sufficient to cause significant progressive vapour condensation along the column length and it will not be possible to predict separating power because of the resultant diminution in vapour velocity. A mean value of boilup rate may be assumed from knowledge of the reflux flow rates at the top and bottom of the column and thereby a mean value of HETP can be predicted, if the heat loss is not too large.

2.2.2.3. Reflux distribution.

The importance of reflux division has been made clear in an earlier section. However, it is equally important to ensure that any wetted surface is uniformly wetted at all boilup rates otherwise the assumption of known interfacial area will be invalidated and the column performance will deteriorate sharply. To ensure this, the distillation column must be vertically mounted and the condenser/

condenser should discharge the reflux over a horizontal weir edge or onto some device which will distribute the reflux evenly. The presence of a contaminant such as silicone grease can cause the liquid film to break up completely into droplets. Rivulet channelling will also occur if the test mixture is negative in the terminology of Zuiderweg and Harmans (10) and the surface tension of the more volatile component is greater. In the work presently under discussion this channelling will not occur as a result of surface tension differences, since both test-mixtures under consideration are neutral.

2.2.3. Previous experimental data.

The work done with columns used by Naragon and Lewis (11), Donnel and Kennedy (12) and Hall and Palkin (13) will now be assessed and compared with the theory of Westhaver.

2.2.3.1. The work of Naragon & Lewis.

Naragon and Lewis (11) described the construction and operat-:ion of a concentric tube fractionating column, 30.5 cm. in length with inner and outer tube radii of r_1 = 0.32 cm. and r_0 = 0.40 cm. Especial care was taken to ensure even division of reflux between the inner and outer walls. n-Heptane/methylcyclohexane was used as test mixture.

Boilup rates were varied between 77.0 ml/hr. and 122 ml/hr. and were determined by measuring the drip rate into the stillpot. However, there is evidence of heat loss, as the authors observed only a minute amount of reflux in the condenser at the lowest rate of 77 ml/hr: from a consideration of the column design it is likely that/

FIG.2.1

Distillation data of Naragon (12).

HETP (cm) v. Boil-up Rate (ml/hr)

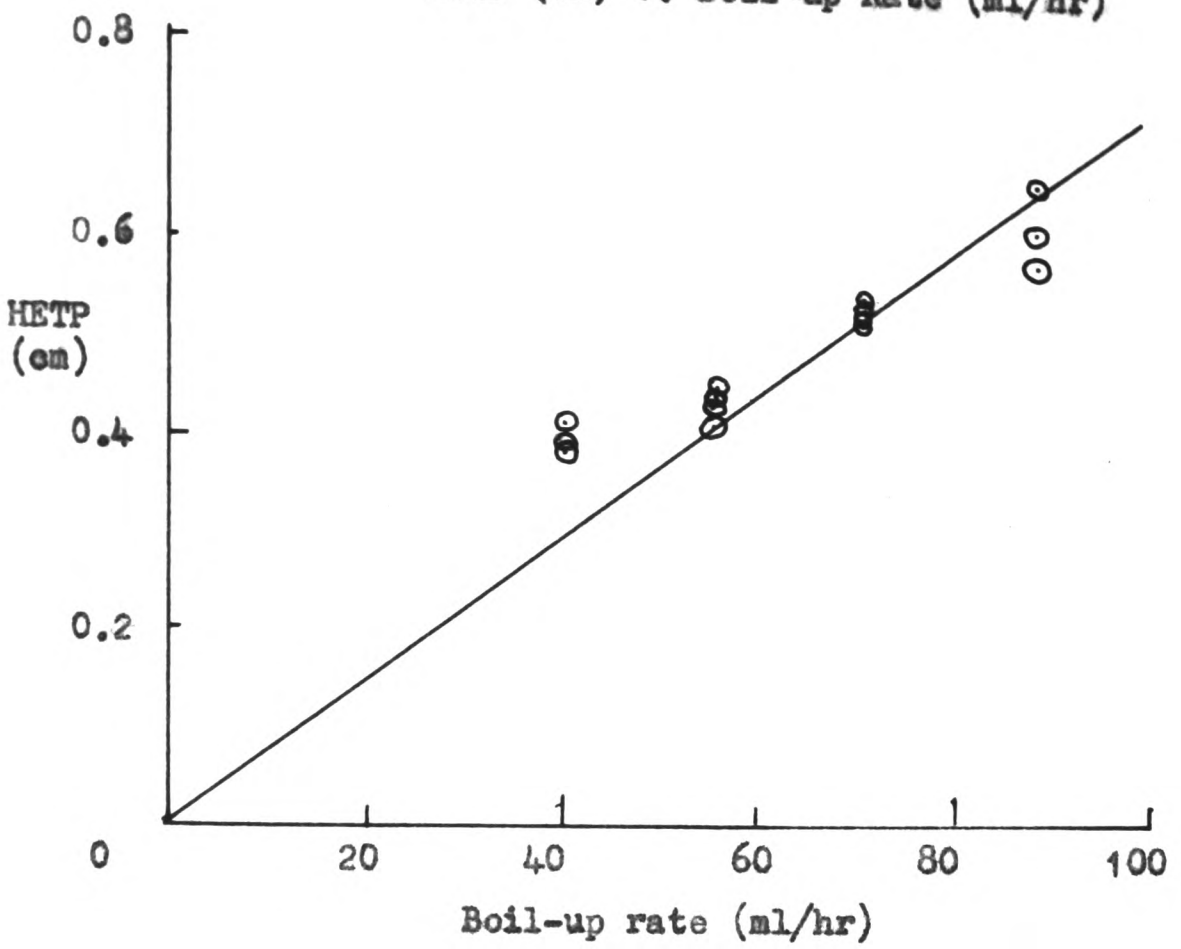
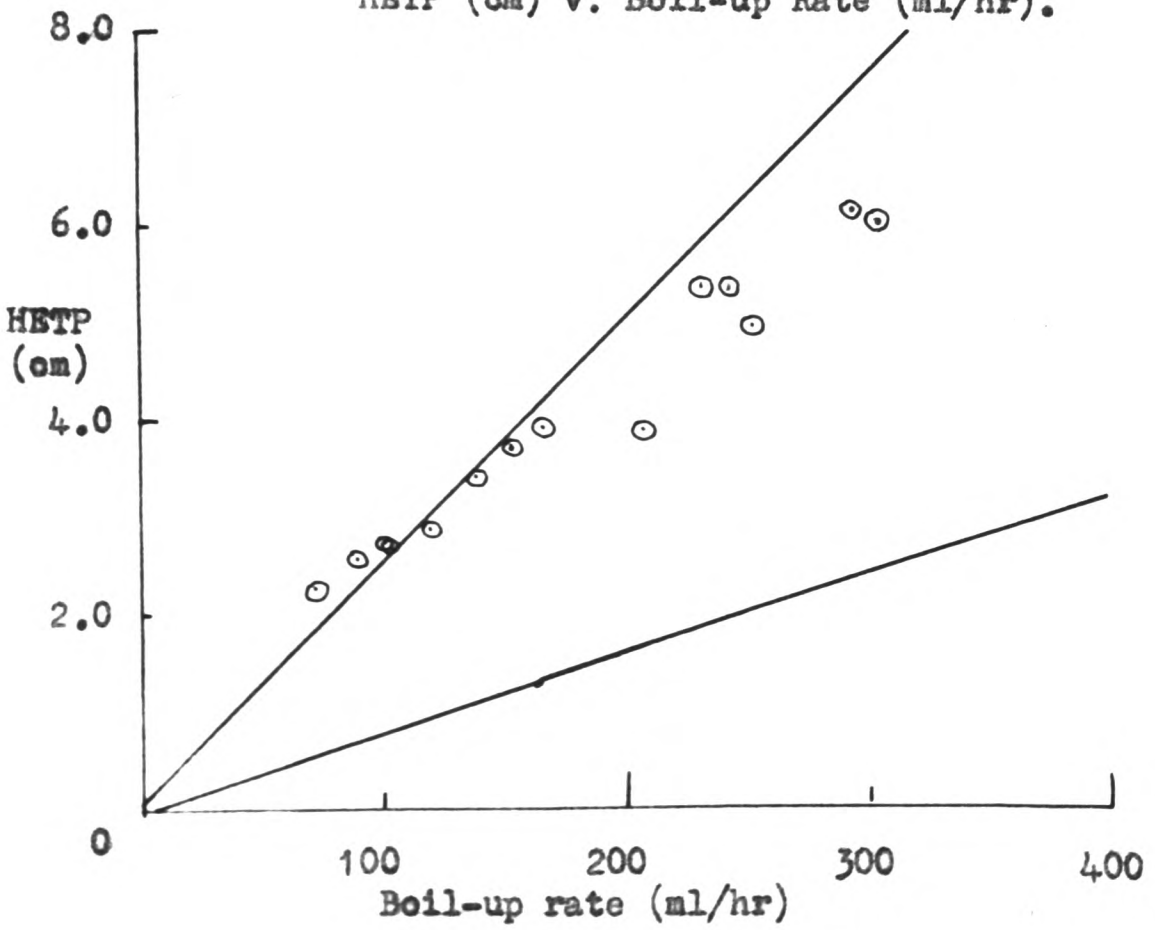


FIG.2.2

Distillation data of Hall and Palkin (13)

HETP (cm) v. Boil-up Rate (ml/hr).



that this heat loss was through the lagged vacuum jacket surrounding the rectifying section.

Assuming the reflux rate at the top of the column at the lowest heat input was c. 5 ml/hr., mean boilup rates were from 41 - 84 ml/hr., a twofold range. Reproducibility of separating power measurements varied from ± 4.0% at the lowest to ± 7% at the highest boilup rates. Apart from the lowest boilup rate values, the results do not conflict with Westhaver theory and are shown opposite in fig. 2.1. However, it must be remembered that mean values of boilup rate have been used, so the results must be treated with caution. It is a pity the authors did not eliminate this slight heat loss, in view of the precautions which were taken to ensure equal division of reflux.

2.2.3.2. Hall and Palkin.

Hall and Palkin used a concentric tube distillation column 238 cm. in length with inner and outer tube radii of r_1 = 0.5 cm. and r_0 = 0.65 cm. The column was constructed so that all the reflux was returned to the inner tube which was made of interlocking tube segments whose surface was wound with a fine glass thread which promoted even circumferential reflux distribution. Like Naragon and Lewis, they used n-heptane/methylcyclohexane as test-mixture. Boilup rates were varied between 75 - 300 ml/hr., as measured by counting the drip rate at the top of the column. Radial heat loss was minimised by means of an air jacket and magnesia lagging. The results are shown opposite in Fig. 2.2, together with the theoretical curve for one wall wetted which is drawn using the experimental/

experimental data of Naragon and Lewis, assuming their corrected values represent the case of both walls wetted. The separating power at low boilup rate is poorer than predicted and this may be due to the estimations of boilup rate having been erroneously low. These rates were measured by counting the drip rate at the top of the column and there is known to have been slight heat loss. On this basis, the results at high boilup rates are better than predicted for one wall wetted and the large scatter suggests that reflux was present on both walls in some of the tests.

Donnel and Kennedy (12) conducted distillation in a column 94 cm. in length with inner and outer radii of $r_1 = 0.63$ and $r_0 = 0.70$ giving annular gap width b = 0.075 cm. In constructing the column they used the method of Naragon and Lewis to ensure that the gap width was uniform. The boilup rate was varied between 35 and 160 ml/hr. For the work at lower boilup rates (34-61 ml/hr.) a test-mixture of 224 trimethylpentane/methylcyclohexane was used, and for the higher values n-heptane/methylcyclohexane was used. The authors claim that at intermediate boilup rates, there was no difference in separating power between the test mixtures for the same boilup rate although no relevant results are given in support of this. The few results obtained under adiabatic conditions are either as good as, or slightly better than those predicted for one wall wetted. Other results which gave slightly better values of separating power were obtained with a controlled heat leak.

Of these three columns investigated, only in the first two cases namely that of Naragon and Lewis, and of Hall and Palkin was close attention paid to the problem of reflux division.

Unfortunately/

Unfortunately, in both these cases, there is evidence of heat loss in the column operation so it is not possible to state conclusively that the theory of Westhaver has been verified. However, on their evidence it can be stated that these results are not in disagreement with the theory of Westhaver. The experimental data of these three workers illustrates the difficulty of providing positive verification of the theory of Westhaver.

Certain experimental data have been obtained from rotary concentric tube fractionating columns with the inner cylinder stationary. These data are more conveniently grouped with the other data obtained with the inner cylinder rotating.

2.3. Columns with the inner cylinder rotating.

Rotating the inner cylinder of a concentric tube column can have two effects:

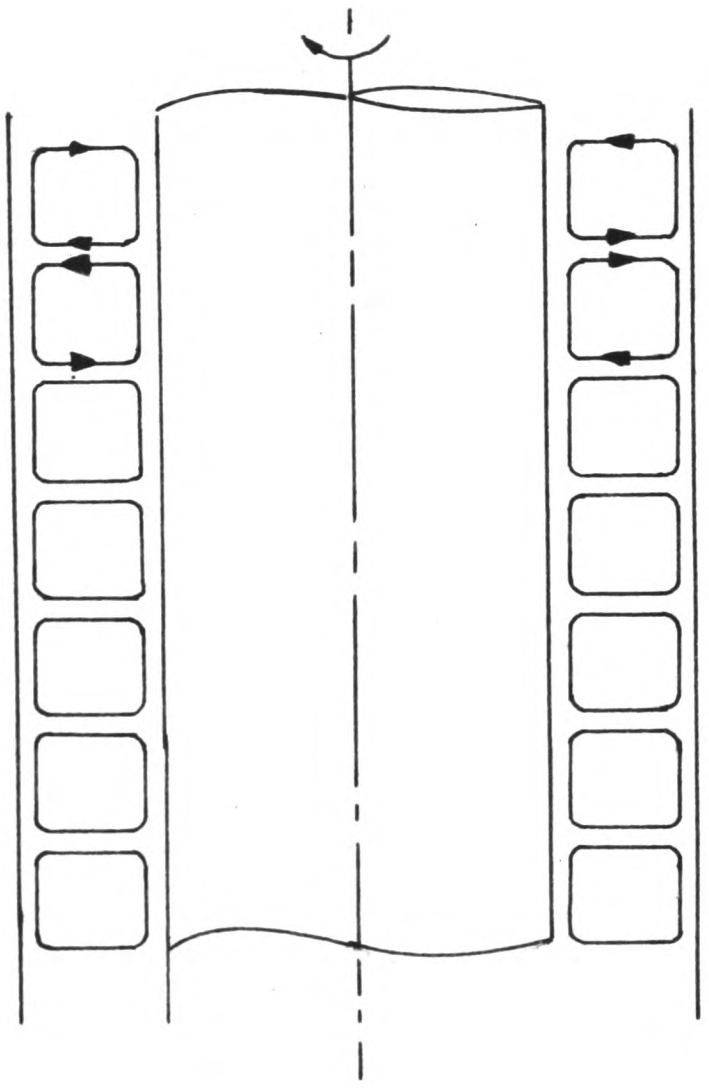
i) Reflux will be thrown off leaving the rotor surface substantially dry.

ii) The vapour in the annulus will have its flow pattern altered in a predictable fashion.

The first of these effects eliminates any uncertainty due to the possibility of unequal reflux division, and the second improves the column performance in terms of separating power, provided that the major proportion of resistance to mass transfer is in the vapour phase. A new independent variable is thus introduced into the system, namely the rotor speed, which should have a predictable effect on separating power. Above a certain rotor speed, the improvement in separating power should more than compensate for the loss/

FIG.2.3

Vortex flow patterns in an annulus.



loss caused by restricting reflux to one surface by the centrifugal action of the rotor.

Before proceeding to a discussion of results obtained from such columns a brief resumé of fluid flow and mass transfer phenomena in rotary concentric tube equipment is presented.

2.3.1. Fluid motion between rotating concentric cylinders.

2.3.1.1. Absence of axial flow.

In a concentric cylinder system, rotation of the inner cylinder above a certain critical speed causes the motion of the fluid occupying the annulus to depart from a laminar motion to regular axisymmetric flow consisting of vortices which rotate in pairs (Fig. 2.3.). These vortices are called Taylor vortices. Taylor (14, 15) predicted and confirmed experimentally that the critical rotational speed for small annular gaps (defined as $b/r_m < 0.3$) is given by:-

$$Ta_c = 41.2$$

where Ta is defined:

$$Ta = \frac{\omega r_1 b}{\nu} \left(\frac{b}{r_o}\right)^{\frac{1}{2}}$$

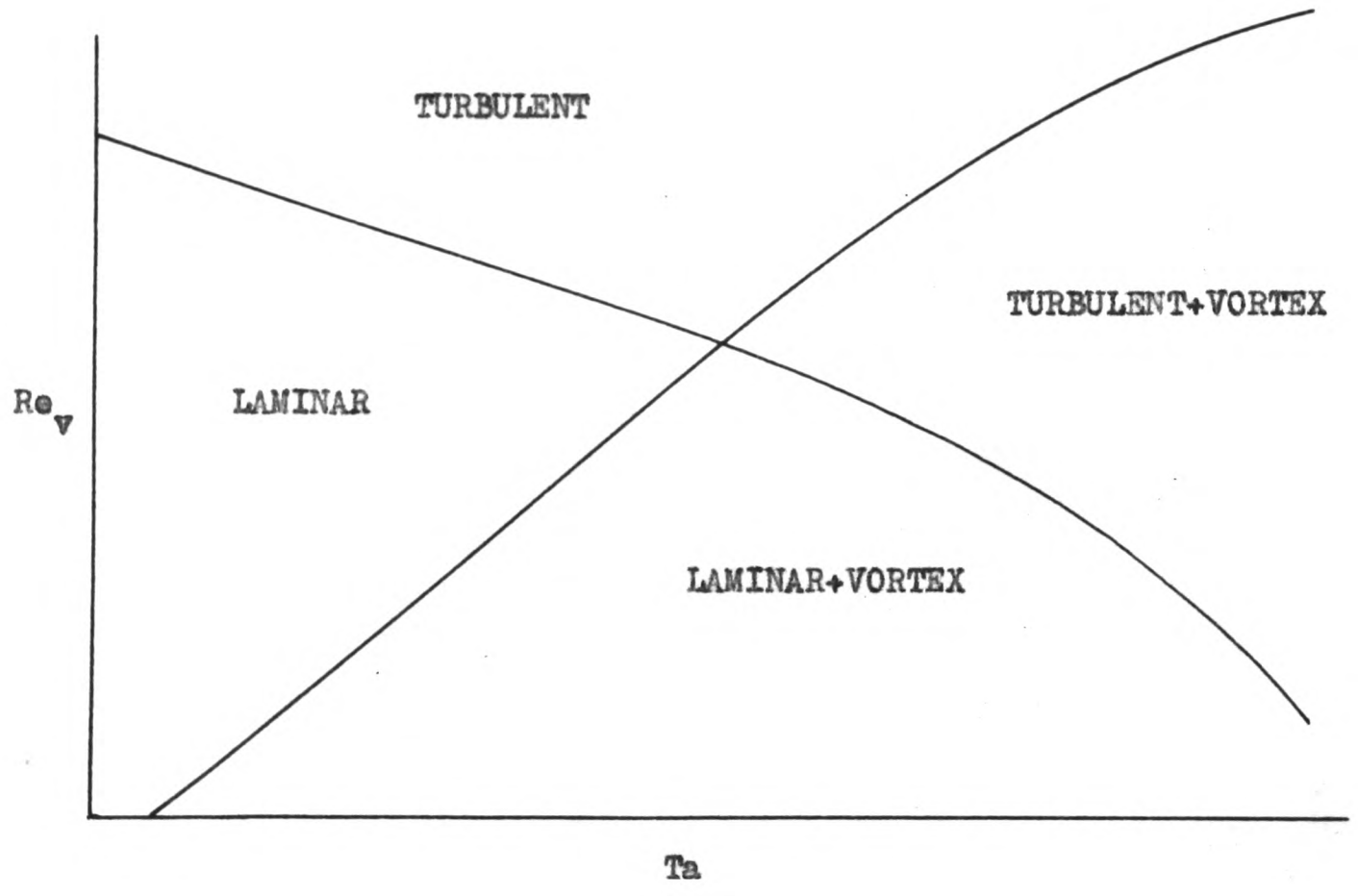
2.3.1.2. With axial flow.

At a sufficiently high rotor speed with low axial flow, bands or rings of vortices can be observed moving with the stream.

As/

FIG.2.4

Flow regimes in an annulus with axial and circumferential motion



As the axial flow rate is increased the angle of tilt of these bands increases, and they pass from a 'flowing ring' to a 'flowing spiral' form. Alternatively if the axial flow rate is held constant, and the rotor speed increased from a low value, the fluid motion changes from laminar to laminar + vortex above a critical speed. The greater the axial flow rate the larger will be the critical rotor speed (or Ta) at which the transition occurs. In all, at least four distinct regimes of vapour flow have been defined: laminar; laminar + vortex; turbulent; turbulent + vortex. A diagrammatic plot illustrating the regimes is shown opposite.

In this case of axial and rotational flow between coaxial rotating cylinders, there are five variables (ω, u, b, r, ν) and the greatest number of these that will not form a dimensionless group is two (since two fundamental dimensions are involved). Three dimensionless groups are therefore necessary to define the fluid mechanics in such a system. These three groups can be:

$$Ta = \frac{\omega r_1 b}{\nu} \quad \frac{b}{r_o}$$

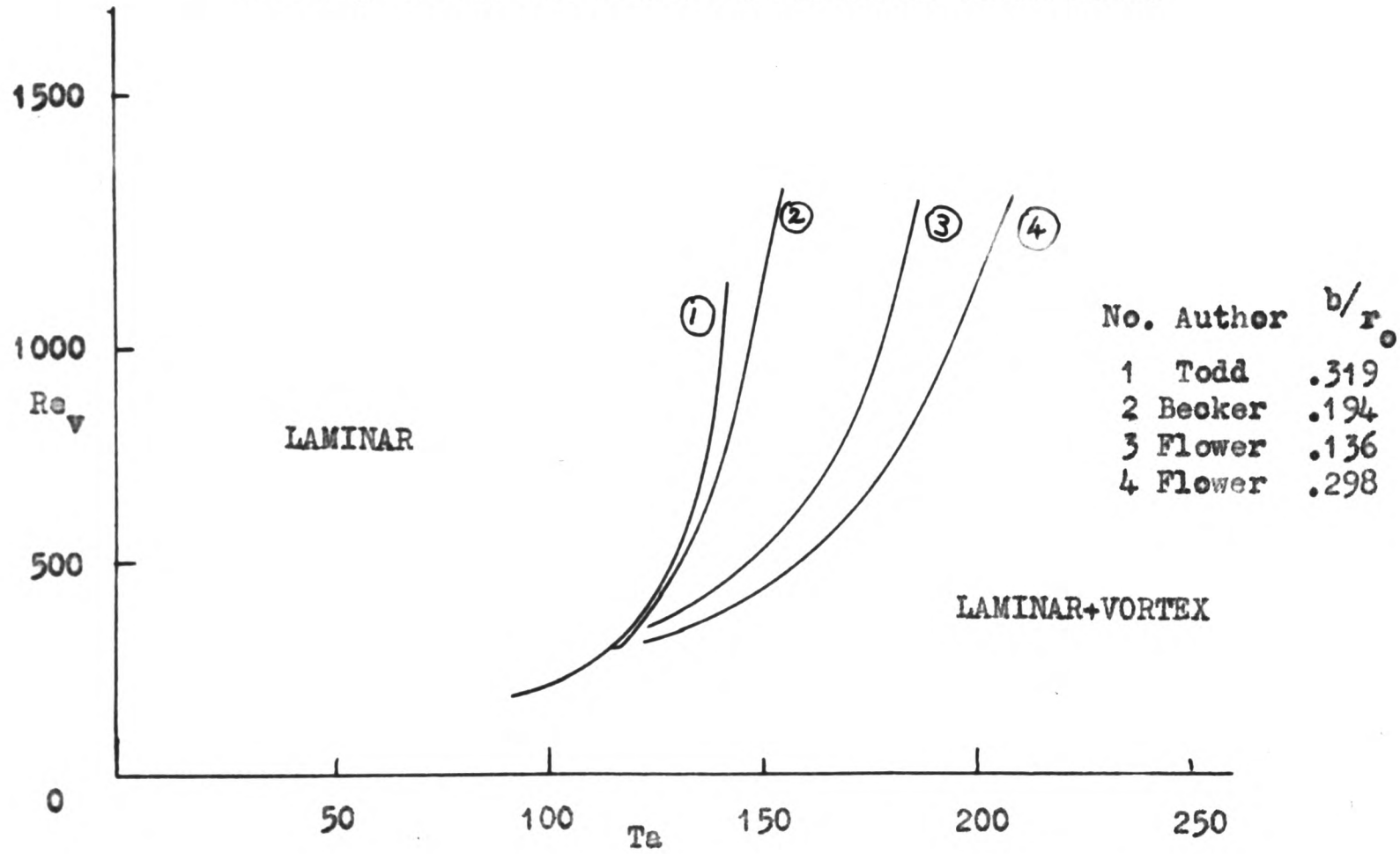
$$Re = \frac{2 u b}{\nu}$$

$$\text{Geometric factor} = \frac{b}{r_o}$$

In/

FIG.2.5

Stability curves for laminar to laminar+vortex flow.



In principle, then, for comparison of two sets of data from different rotating concentric cylinder systems, these should be geometrically similar with the same $^{b}/_{r_o}$. Each transition curve shown in Fig. 2.4 is therefore a member of a family of such curves, each corresponding to a different value of $^{b}/_{r_o}$. In practice, however, the work of Flower (22) has established that the position of the laminar/laminar + vortex transition curve is only very weakly dependent on the value of $^{b}/_{r_o}$ when the data are plotted in the manner of Fig. 2.4 so that a single curve of Ta versus Re can represent this transition for a wide range of $^{b}/_{r_o}$ values within the limits of experimental error. The transition data for laminar-laminar + vortex flow of Becker (16), Flower (22) and Todd (23) are plotted in Fig. 2.5.

2.3.2. Laminar + vortex flow.

In the operation of rotary fractionating columns, the laminar + vortex regime is of principal interest. Mass, heat and momentum transfer data obtained from similar systems lead to the expectation that in the fractionating columns used in the present investigations and in those recorded in the literature:

i) the vapour motion will be laminar + vortex over a wide range of operating variables

ii) the effect of Ta on separating power ought to be predictable.

2.3.3. Dependence of Nu on Ta in laminar + vortex regime.

From appropriate heat and mass transfer measurements it has been shown that:

Nu/

$$Nu \propto (Ta)^{0.5} \qquad (2.4)$$

$$\text{or} \quad Sh \propto (Ta)^{0.5} \qquad (2.5)$$

Bjorklund and Kays[17] obtained a heat transfer correlation which reduces to:

$$Nu \propto (Ta)^{0.5} \left(\frac{r_0}{r_1}\right)^{0.25}.$$

Gazley (18) and Becker (16) obtained similar values for the Ta exponent although Haas and Nissen (19) found when water was used as the heat transfer medium:

$$Nu \propto (Ta)^{0.22}.$$

Replacing the water by air gave a relation similar to equation 2.4. Tachibana, Fukui and Mitsumura (20) varied Pr by using oil and air. They also varied b/r_1 between $0.0323 < b/r_1 < 0.256$ and found:

$$Nu = 0.422\,(Ta)^{0.5} \left(\frac{r_0}{r_1}\right)^{0.25} (Pr)^{1/4}.$$

Mass transfer investigations have yielded similar correlations. In his mercury vapour transfer work, Shahbenderian found

$$Sh = 0.45\,(Ta)^{0.5} \left(\frac{r_0}{r_1}\right)^{0.25}.$$

Results of Vaporization studies described in an anonymous 'Shell' report (24) showed a similar relation.

Although at higher values of Ta ($Ta > 1000$) when in the laminar/

laminar + vortex regime, Flower (22) noted that the Ta exponent fell to a low value of 0.3. He points out that this effect might be due to abnormal depression of the liquid surface temperature caused by high evaporation rates at high Ta. The mass transfer work of Todd (23) supports equation 2.5.

Batchelor (25) found that within the laminar + vortex regime a momentum transfer relationship similar to those for mass and heat transfer is obeyed. He also advanced a theoretical argument in explanation of the dependence of torque upon the square root of Ta in this regime. Shahbenderian extends this argument by assuming that the thicknesses of the momentum and mass transfer boundary layers are the same and derives an expression for separating power:

$$N = 2\,(Ta)^{0.5} \left(\frac{r_0}{r_1}\right)^{0.25} \frac{1}{(Re)\,(Sc)} \frac{1}{W_1}$$

In spite of some arguable assumptions in this analysis, it appears likely from the experimental data presented above that:

$$N \propto \frac{1}{b} (Ta)^{0.5} (Re)^{-1} \left(\frac{r_0}{r_1}\right)^{0.25} \frac{1}{f(Sc)}$$

or that

$$\frac{H}{b} \propto (Re)\,(Ta)^{-0.5} \left(\frac{r_1}{r_0}\right)^{0.25} f(Sc) \qquad (2.6)$$

It should thus be possible to compare individual workers experimental data with values of H predicted from the above relation.

2.3.4./

2.3.4. Previous distillation work with rotating concentric cylinder columns.

2.3.4.1. Willingham et al.

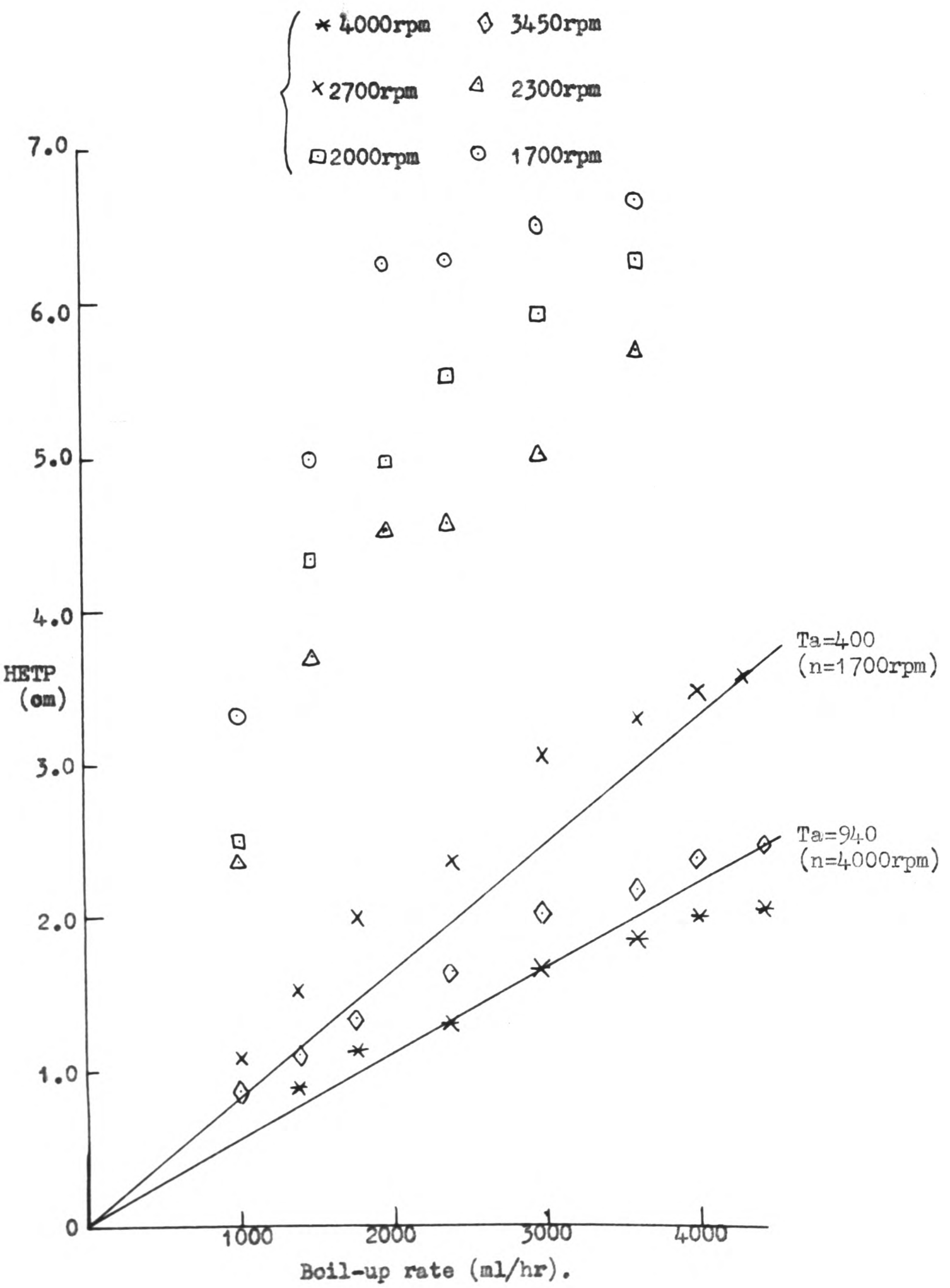
Willingham et al (4) described the construction and performance of a rotary concentric tube distillation column with rectifying section 58.4 cm. in length and inner and outer tube radii r_1 = 3.72 cm. r_0 = 3.83 cm. and annular gap of 0.109 cm., giving a b/r_0 = 0.029. The test mixture used was 2.2.4 trimethyl-:pentane/methylcyclohexane. Vapour was condensed at the stillhead by a main condenser and a side-condenser. This condensate flowed through the upper rotor bearing and through six holes drilled in the bearing mounting plate: no precautions were taken to ensure that reflux was evenly distributed around the outer tube surface. Heat loss from the rectifying section was minimised by the provision of three Nichrome heating elements surrounded by thermal insulation which were used to maintain appropriate temperatures in conjunction with thermocouples.

The column performance was investigated over the ranges boilup rate 1000-4000 ml/hr. and rotor speed 1750-4000 rpm. which correspond to $140 < Re < 560$ and $400 < Ta < 940$ respectively, assuming the vapour kinematic viscosity ν = 0.0306 cm^2/sec. This means that the vapour flow was in the laminar + vortex regime throughout, assuming that the data in fig. 2.5 is correct and the assumed value of ν is roughly correct.

At Ta = 0, the experimental values of separating power were between $2/3$ and $1/2$ the values predicted by Westhaver for one wall wetted. Since no precautions were taken to ensure a uniform reflux/

FIG 2.6

Distillation data of Willingham et al (4).



reflux film (e.g. by the use of a weir or similar device) it is likely that the authors' surmise of poor reflux distribution being responsible for the poor separating power is correct.

The remaining results are shown plotted opposite in Fig.2.6. At higher values of Ta (Ta > 600 - n > 2700) HETP increases linearly with boilup rate and nowhere is the relationship $H \propto Ta^{-0.5}$ obeyed. Although it is possible to estimate a value of δ_v, it is still not possible to predict absolute values of HETP, as the form of the relation of HETP with Sc is unknown. However since the same test-mixture was used in the present investigation, which is described in detail in Chapter V, it is possible to estimate a value of f(Sc) from the present work. Using the relation given as equation 2.6, absolute values of H can be estimated for various Ta and Re. These estimated values have been plotted with Willingham et al experimental data in fig. 2.6. At the highest rotor speed, Ta = 940, the experimental results agree, but at lower values of Ta the divergence between estimated and experimental data becomes progressively greater. Moreover, at lower rotor speeds (Ta < 540; n < 2300 rpm.) the variation of H with boilup rate is no longer a straight line at constant Ta.

Assuming that the distribution of liquid reflux is uniform, (which is likely at the rotational speeds used since with the narrow gap width the vapour drag will be sufficient to spread the liquid evenly) and that the rotor surface is substantially dry (as most reflux will be flung off by centrifugal action), these results are surprising. It is possible, however, that under certain conditions/

conditions of operation there is liquid side resistance to mass transfer present. This point will be amplified in Chapter V, when the results of the present experimental investigation are assessed.

2.3.4.2. Results of Sladacek.

Sladacek (5) described experiments on a rotary concentric tube distillation column cm. in length and outer tube radius r_o = 1.61 cm. Into this tube could be inserted each of 3 rotors to give inner tube radii of r_i = 1.34 cm., 1.41 cm. and 1.51 cm. respectively. These three rotors gave b/r_o = 0.168, 0.124 and 0.062 respectively. The boilup rate was constant at 600 ml./hr. which is equivalent to Re = 230, assuming vapour kinematic viscosity of ν = 0.031 cm^2/sec. Rotor speeds were varied over the range 3500-8500 r.p.m. by means of a variable frequency generator driving a 'canned' squirrel-cage rotor. This speed range gave Ta in the range C.400-4000. overall. The test mixture used was n-heptane/ methylcyclohexane. Heat loss from the column wall was controlled by an arrangement of 3 jacket heaters and resistance thermometers and the temperature on the outer wall of the stator was maintained at 1.0-1.2°C lower than the boiling point of the liquid.

The test mixture used by Sladacek was not the same as that used in the present investigation so it is not possible to estimate accurately the value of f(Sc) in equation 2.6 as was the case with the results of Willingham et al, and hence the values of H_v corresponding to those obtained from Sladacek's operating conditions cannot be predicted. However, it is unlikely that values of vapour/

conditions of operation there is liquid side resistance to mass transfer present. This point will be amplified in Chapter V, when the results of the present experimental investigation are assessed.

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vapour diffusivity and kinematic viscosity of the two test mixtures concerned differ significantly, so it is possible to make some estimate of values of H_V. Assuming similar values of Sc for the two systems and a laminar + vortex flow regime, values of H_V were calculated and compared with the experimental data of Sladacek. In contrast to the results of Willingham et al., all Sladacek's values of H_V are an order of magnitude higher than those predicted; also the experimental value of the separating power using b/r_o = 0.168 at rotor speed of 5100 rpm. is only as good as that predicted for both walls equally wetted by reflux with the rotor stationary. As the heat leak from the column (referred to above) may be expected to cause the measured separating power to be better than that predicted on the basis of adiabatic operation, it is therefore likely that there was some fundamental fault inherent in the operation of this column, such as an electrical heating effect produced in the rotor. It is not likely that at these values of Ta and Re there is such a massive liquid side resistance as could account for the difference between the estimated and actual values of H_V.

2.3.4.3. Results of Matterson; relative importance of liquid and vapour phase resistance.

Macleod and Matterson (1, 2) designed and tested a rotary concentric tube column which had no rotating shaft seals and no bearings exposed to hydrocarbon vapour. It was 66 cm. in length with an outer tube radius r_o = 1.40 cm. and rotor of radius r_1 = 1.07 cm. This rotor was made of copper so that fins or wires could be attached in order to stir the vapour or liquid as required.

In/

In this way the relative contributions of the vapour and liquid side resistance to mass transfer were investigated over a range of boilup rates 200 ml./hr. - 800 ml/hr. at 1470 rotor r.p.m. using a text mixture of n-heptane-methylcyclohexane. These corresponded to $85 < Re < 310$ and $Ta = 830$, assuming $\nu = 0.031$ cm^2/sec. Under these operating conditions, it was demonstrated that the contribution of liquid side resistance was negligible.

2.3.4.4. Results of Matterson and Shahbenderian.

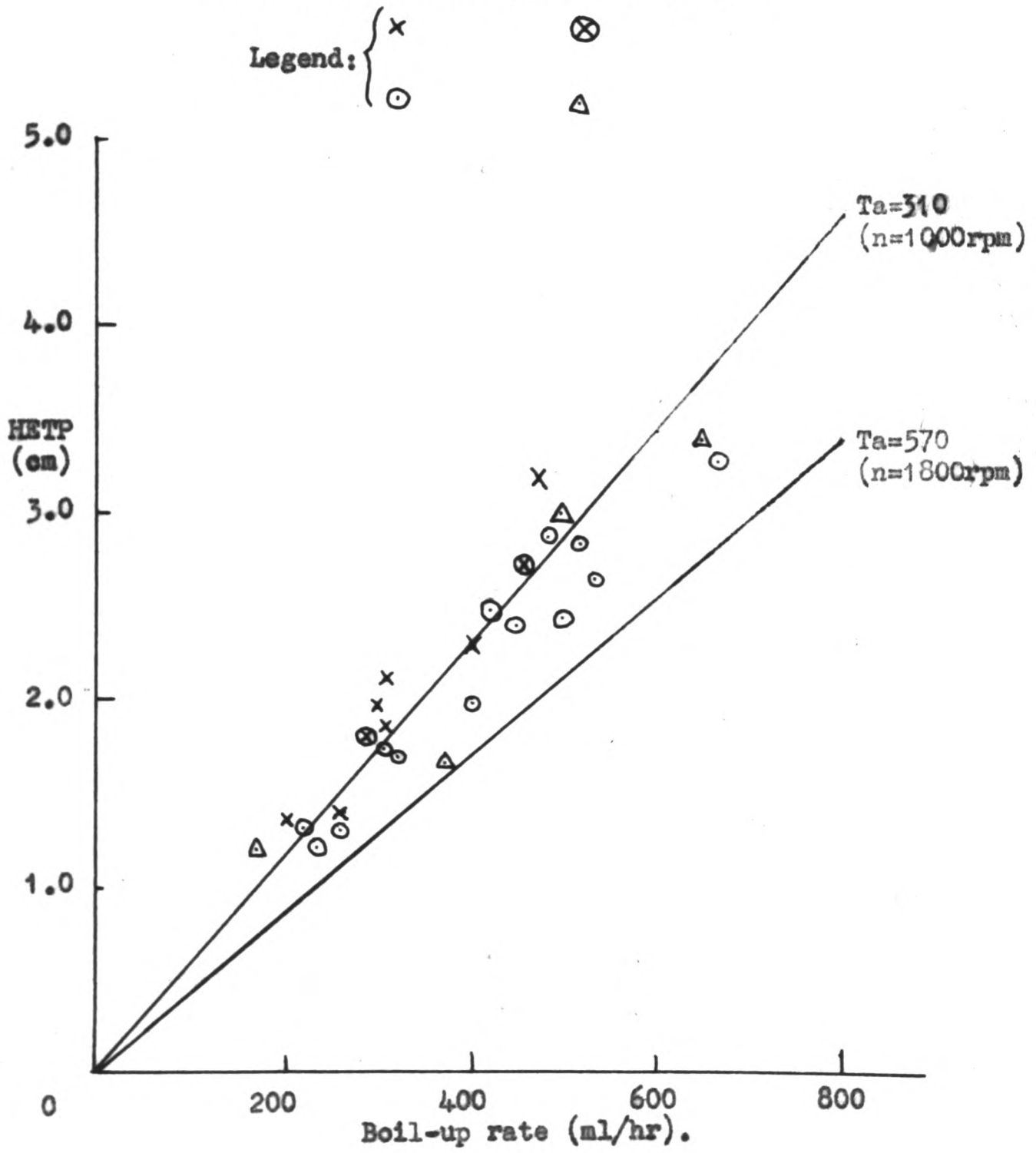
The remainder of their experiments were conducted with each of two smooth rotors of radii $r_1 = 1.28$ cm. and $r_1 = 1.07$ cm. and were similar to, though more limited in scope, than those of Shahbenderian (3) who used a large rotor $r_1 = 1.30$ cm., intermediate rotor of 1.20 cm. and the small rotor used by Matterson in the same distillation column with the same test mixture. In addition, Shahbenderian extended the rotor speeds from the single speed of 1470 r.p.m. to give a range from 300-2850 r.p.m. by using a variable frequency generator. Because of the mechanical design, it was not possible to work in the speed ranges 600 ± 100 r.p.m. and 1200 ± 200 r.p.m.

Experiments were conducted with the rotors stationary and rotating between boilup rates of .200 ml./hr. and .800 ml./hr. There was considerable experimental scatter with the rotor stationary. With the large diameter rotor the results are roughly equivalent to those predicted by the Westhaver equation for one wall wetted assuming a value $D_v = 0.031$ cm^2/sec. (This value can be deduced from the results of Naragon and Lewis for both walls wetted). With the intermediate rotor, it is apparent that both surfaces/

FIG.2.7

Distillation data of Shahbenderian (3). 1.20cm. rotor.

HETP (cm) v. Boil-up Rate (ml/hr).



surfaces were wetted to some degree, as all results are better than those predicted for one wall wetted. With the smallest rotor, which was made of copper (the other two were glass) both surfaces are apparently equally wetted as the results corresponded with those predicted from both walls wetted theory. Accepting that a uniform reflux film could be formed on the outer glass surface, improved heat transfer between the copper rotor and the condenser could account for a possible film of reflux forming on the copper surface.

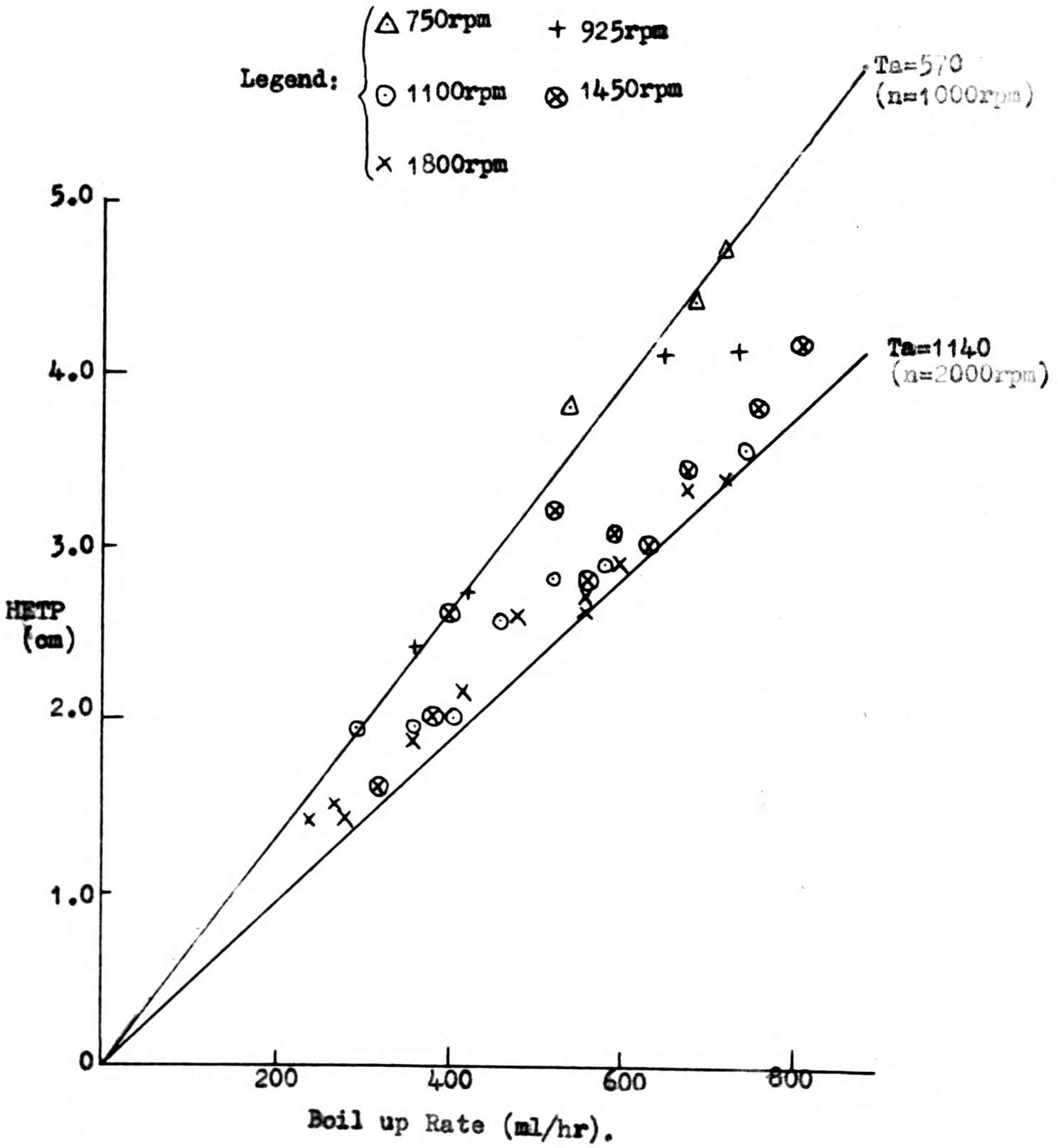
With the largest diameter rotor, Shahbenderian worked in the speed range 80-300 r.p.m., which corresponds to $9 < Ta < 32$. According to fig. 2.5, the vapour flow will not be laminar + vortex. It is not therefore possible to compare these results with those predicted by equation 2.6. Even at the speed of 1470 r.p.m. corresponding to Ta = 157 used by Matterson, it is possible the vapour flow is still laminar.

With the intermediate size rotor $r_1 = 1.20$ cm., Shahbenderian investigated column performance in the speed range 400-2450 r.p.m. which corresponded to $125 < Ta < 775$ with boilup rates from 200-800 ml./hr. ($90 < Re < 355$). His later experiments were conducted with a string wiper attached to the upper end of the rotor: using this device, Shahbenderian observed a significant improvement in column performance. At the lowest rotor speed of 400 r.p.m. (Ta = 125) the vapour flow will still be laminar according to the transition curve in Fig. 2.5, and the rotor speed was most likely to be insufficient to throw off reflux. Accordingly, only/

FIG.2.8

Distillation data of Shahbenderian (3) . 1.07 cm. rotor.

HETP (cm) v. Boil -up Rate (ml/hr).



only those results obtained (in the laminar + vortex vapour regime) at speeds between 1000-2450 r.p.m. ($310 < Ta < 775$) are shown in Fig. 2.7 and are compared with values of H estimated from the present work. These values of H are predicted assuming that the n-heptane/methyl-cyclohexane test mixture has values of λ_v and ν similar to those of 224 trimethylpentane/methylcyclohexane which was used in the present work. Allowing for the large scatter present, the values of H obtained at 1000, 1500 and 1800 r.p.m. are not in disagreement with estimated values. The few values obtained at 2450 r.p.m. are more scattered and are poorer than those predicted. At boilup rates below 200 ml./hr. values of H are more scattered and are higher than those at > 200 ml./hr. presumably due to dry patches on the stator wall arising from the very low wetting rate.

With the small copper rotor (r_1 = 1.07 cm.) Shahbenderian investigated separating power over similar speed ranges (300-2100 r.p.m.) and the same boilup rates. Because of the wider gap width these corresponded to $120 < Ta < 840$ and $94 < Re < 375$. Only those results obtained at rotor speeds > 700 r.p.m. are presented in Fig. 2.8 because of a possible wet rotor surface at lower speeds.

At speeds of 750 r.p.m. and 925 r.p.m., the scatter is remarkably large for all values of H at Q < 500 ml./hr. This Shahbenderian presumed arose from uneven wetting of the stator. Leaving aside these anomalous results, values of separating power at 1000 r.p.m. are c.40% better than predicted and those at 1450 r.p.m. c.20% better while at 1800 r.p.m. they agree with those estimated from theory. As before, the experimental scatter is large.

Included/

Included are the few results of Matterson obtained at 1470 r.p.m.

The reason for the apparent improvement over theory at the lower rotor speeds and the lack of dependence of H on Ta is not clear. In contrast with conditions prevailing when the intermediate glass rotor was used, the copper rotor may conduct heat more efficiently and cause the occurrence of non-adiabatic conditions at the top end of the rectifying section. However, there is no good reason why the performance should be as predicted at a rotor speed of 1800 r.p.m.

2.3.5. Summary.

Summarizing the experimental results of Willingham, Sladacek and Shahbenderian, those of Willingham agree with the Westhaver and Shahbenderian theory only at the highest rotational speed, using data from the present investigation. The possibility of liquid side resistance cannot be discounted and is further considered in this connextion in Chapter V. It is most likely that there was some fault in the distillation column used by Sladacek as the experimental values of H were an order of magnitude greater than those estimated. The limited tests of Shahbenderian cannot be said to contradict the theory in the L + V regime, and departures from theory using the copper rotor may be due to non-adiabatic operation.

To test the Westhaver Shahbenderian theory more extensively and to provide possible design data for rotary concentric tube fractionating columns, further experimental work was conducted by the present author, the results of which are presented and assessed in Chapter V.

CHAPTER III

In this chapter, the requirements for a test mixture are presented, then these points are developed and discussed at length. The available literature is then reviewed , and test mixtures suitable for use in fractionating columns of high separating power at atmospheric and sub-atmospheric pressures are suggested.

3.1. Properties of test mixture.

To be suitable for evaluating a distillation column, a binary mixture should have the following properties:

(i) Each component should be available in as pure a condition as possible.

(ii) At the operating pressure, the boiling point should be in the range 90°C to 140°C.

(iii) The system should be ideal with a constant relative volatility, and no azeotropes should be formed.

(iv) The chemical and physical properties of each component must be similar

(v) A convenient analytical method should be available.

(vi) The relative volatility, α, should be appropriate to the separating power of the column.

3.1.1. Purity

Impurities present in a binary mixture can produce two unwanted effects; the vapour-liquid equilibrium of the system may be affected, thereby causing the relative volatility to be altered from the correct value and possibly also resulting in the relative volatility varying with mole fraction; the physical property which is used for determining the composition of the binary may be affected, giving erroneous values of stillpot and distillate concentrations.

Purity can usually be checked by comparison of the experimentally obtained and literature values of the commoner physical properties such as boiling point, freezing point, refractive index and density. However, more sophisticated techniques based on gas chromatography have recently become available. By such a method, amounts of impurity which differ only very slightly in physical properties from the pure material under test may be detected. Since hydrocarbons are notoriously difficult to purify, and are commonly used as test-mixture components, gas chromatography presents an ideal means of detecting impurities. Although it is unlikely that the physical properties of the components would be affected by impurities which are undetected by conventional types of test, it is nevertheless possible that vapour liquid equilibrium values might be altered by these.

3.1.2. Boiling point range

It is advisable to choose materials which will have boiling points in the range 90°C - 140°C at the operating pressure. If the boiling point of either component lies much below 90°C condensing the vapours at the stillhead becomes difficult. Above 140°C, the risk of thermal decomposition due to excessive local overheating in the stillpot arises.

3.1.3. Relative volatility and ideality

Consider an ideal binary system whose vapour and liquid phases are in equilibrium at constant temperature. It can be shown from Raoult's Law and Dalton's Law that the relative volatility, α, can be written:

$$\alpha = \frac{P_1}{P_2} \qquad (3.1)$$

or

$$\alpha = \frac{y(1-x)}{x(1-y)} \qquad (3.2)$$

where P_1, P_2 are the vapour pressures of the pure components, x and y are the liquid and vapour mole fractions of the more volatile component.

The volatility of each component is defined as the ratio of the partial pressure to the mole fraction. These derivations can be seen in a good text-book on the subject, for example, Hala, Pick, Vilim (26).

At constant pressure equation (3.1) is not necessarily true, as the vapour pressures alter with temperature: if the system is close-boiling and the relative volatility close to unity, the vapour pressure ratios will probably vary only by a very small amount, so α will remain constant.

The relative volatility is best determined by vapour-liquid equilibrium measurements, obtained by using a suitable circulating still such as an Othmer still. It is necessary to ensure that the pressure and temperature are accurately controlled, and care must be taken to eliminate errors due to partial condensation of vapour superheating at the still walls, or incomplete mixing in the boiler. Results should always be thermodynamically checked to ensure the absence of systematic errors which may arise from any of the above-mentioned causes. If, however, the relative volatility is low, it may not prove possible to eliminate random errors which arise from insufficiently accurate analytical determinations, so it will not be possible to apply a thermodynamic test for systematic

errors. In an effort to improve the accuracy, various workers (27 , 28) have developed a twoplate still.

When the mole fraction of either constituent falls much below 15%, equation (3.2) for calculating α becomes much more sensitive to small errors in the mole fraction determination, so it is inadvisable to work outside the range $0.15 < x < 0.85$.

3.1.3.2 Importance of constancy of α (Relative volatility).

When a binary mixture is distilled under total reflux in a distillation column with N theoretical plates, this can be shown to be equal to a function of the stillpot and distillate concentrations of the more volatile component, provided the relative volatility remains constant:

$$N = \frac{\log \frac{x_d(1-x_s)}{x_s(1-x_d)}}{\log \alpha} - 1 \qquad (3.3)$$

which is the Fenske equation.

Provided the relative volatility remains constant over the concentration range employed, the Fenske equation can be used for determining the number of theoretical plates, N. If, however, the relative volatility varies, the number of plates can be estimated by graphical construction using an accurately prepared equilibrium diagram. With a close-boiling mixture, which has values of α close to unity this procedure can no longer be used since the equilibrium line and operating line lie very close to each other and the graphical procedure becomes inaccurate. Plate-to-plate calculations then have to be employed, which are tedious and require the use of a digital computer; It is therefore advantageous to choose a system with a constant relative volatility which is accurately known. The following example

shows that when the Fenske equation is used, a small error in α (using a close-boiling test-mixture) gives rise to a large error in N.

A commonly used close-boiling system in use for investigating the performances of high-efficiency columns is n-heptane-methylcyclohexane. Various values of α are reported in the literature ranging from $\alpha = 1.07$, (39, 42) to $\alpha = 1.083$ (33, 40).

Suppose in a particular distillation we obtain a distillate concentration $x_D = 0.85$ resulting from a stillpot concentration of $x_S = 0.25$. From the Fenske equation using $\alpha = 1.07$ we obtain N = 41 plates, while when $\alpha = 1.083$ N = 35 plates. Similarly with $x_D = 0.6$, $x_S = 0.4$, the respective values of N are 18 and 15. For an error of 1.2% in the relative volatility, we obtain errors of 16% to 18% respectively. Attention has been drawn to this difficulty inherent in the use of such systems by Beatty and Calingaert (39), and by Coulson, Hales and Herington (29).

3.1.3.3 Deviations from Raoult's Law

When Raoult's Law is obeyed, the total pressure of a binary system is given by:

$$\pi = x_1 (P_1 - P_2) + P_2 \qquad (3.4)$$

This equation provides a rapid and convenient method for determining whether a system is non-ideal. If the data is obtained at a known pressure π, and accurate vapour-pressure data are available, the total pressure can be computed. If there are appreciable deviations from the measured total pressure, departures from Raoult's Law of one

or both components are indicated. Agreement between computed and measured total pressures does not necessarily mean the system is ideal: a negative deviation in one component may be offset by a positive deviation in the other.

Activity coefficients.

Nearly all systems show some deviations from Raoult's Law. Equation (3.4) above then becomes:

$$\pi = x_1 (\gamma_1 P_1 - \gamma_2 P_2) + \gamma_2 P_2 \qquad (3.5)$$

where γ_1 and γ_2 are the activity coefficients. Although here presented as mere correction factors, a rigorous thermodynamic derivation is given by Wohl (30).

Applying Dalton's Law gives:

$$\frac{y_1}{x_1} = \frac{P_1 \gamma_1}{\pi} \qquad (3.6)$$

Introducing a correction for slight deviations from ideal gas behaviour in the vapour phase gives:

$$\frac{y_1}{x_1} = \frac{P_1 \gamma_1}{\pi z_1} \qquad (3.7)$$

where z_1 is the gas correction factor for component 1, and is defined by:

$$\ln z_1 = \frac{(V_1 - B)(P_1 - \pi)}{RT} \qquad (3.8)$$

As with activity coefficients, gas correction factors are rigorously derived by Wohl.

Activity coefficients may therefore be determined from vapour-liquid equilibrium data provided the total pressure and the vapour pressures of the pure components are known. Usually, vapour pressures can be calculated from the operating temperature by means of a relation such as the

Antoine equation. The activity coefficients may then be used to test equilibrium data for consistent errors.

3.1.3.4 Thermodynamic testing

A suitable thermodynamic consistency test which follows from the Gibbs-Duhem equation was proposed by Redlich and Kister (31).

For a binary system at constant pressure:

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2} \cdot dx = \int_0^1 \frac{H^E}{2.303\,RT^2} \frac{dT}{dx} \cdot dx \qquad (3.9)$$

With close-boiling systems having a relative volatility close to unity, the heat of mixing, H^E , is very small, and so the right hand side of equation (3.9) may be neglected:

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2} \cdot dx = 0 \qquad (3.10)$$

If the logarithm of γ_1/γ_2 is plotted against the liquid mole fraction, the total area under the curve must be zero. If this condition is not fulfilled, then the measured data will not obey the Gibbs-Duhem equation and so are inconsistent.

3.1.4. Physical and Chemical Properties.

The physical and chemical properties of the components of the test mixture should be as similar as possible. This condition is not normally fulfilled perfectly in distillation practice, i.e. a mixture which requires separating will probably not be ideal. Strictly speaking, comparative data for columns of similar type can only be obtained by using an ideal mixture. When the aim is to predict the performance of the column theoretically, it is most important that the vapour viscosities and densities upon which these predictions

depend, change as little as possible. Variations in the liquid viscosity and density will cause changes in the liquid film thickness which will affect the rate of mass transfer. Surface tension variations along the length of the wetted-wall column will result in rivulet channelling of the liquid film if the surface tension of the more volatile component is significantly greater than that of the second component, i.e. if the mixture is negative in the terminology of Zuiderweg and Harmans (10).

3.1.5. Determination of composition.

For determination of the stillpot and distillate concentrations, it is necessary to analyse the small samples of the mixture speedily and accurately. Since the mixture is comprised of two similar substances it is sometimes difficult to find a suitable analytical method, since the chemical and physical properties are alike. Refractive index measurements usually afford the most rapid determination: in cases where the refractive indices are very close measurement of the optical density of the solutions at suitable wavelengths in the ultraviolet region may be employed.

3.1.6. Relative volatility and separating power

As indicated earlier, it is recommended that the stillpot and distillate concentrations should be kept in the ranges $x_s > 0.15$ and $x_b < 0.85$ because of the uncertainties which may exist in equilibrium values at concentration extremities.

By substituting these limiting values in the Fenske equation, the maximum number of plates for which a mixture is suitable can be found. By this criterion, the mixture n-heptane-methylcyclohexane which is assumed to have a value

of α = 1.075 is suitable for testing columns of up to 47 plates, while the mixture 2,2,4 trimethylpentane-methylcyclohexane with an α = 1.049 can be used in columns of up to 70 plates.

In a concentric-tube rotary distillation column which has a wide range of operating conditions, and hence a large variation in N, it is desirable to determine, for any particular test mixture, the smallest number of plates which may be calculated with a particular degree of accuracy, and also the optimum values of stillpot concentration which may be used for the best accuracy for any value of N.

3.1.6.1. Variation in error of N

Let us assume that a small constant error is made in each refractive index measurement and that the dependence of mole fraction on refractive index is linear. For a given value of N, it can be shown that to attain the lowest possible error in N, the stillpot concentration should be chosen so that the distillate concentration lies as far above 0.5 as the stillpot concentration lies below 0.5, or, in mathematical terms:

$$x_s + x_D = 1$$

In most cases, however, the relation between refractive index and concentration is quadratic, and the minimum error for any given N is then obtained when:

$$x_s + x_D = A$$

The sum of stillpot and distillate concentrations, A, will usually lie between 0.9 and 1.0, and increase with increasing N.

FIG. 3.1

Minimum error curve for n-heptane/methylcyclohexane
(%age error v. No. theoretical plates)

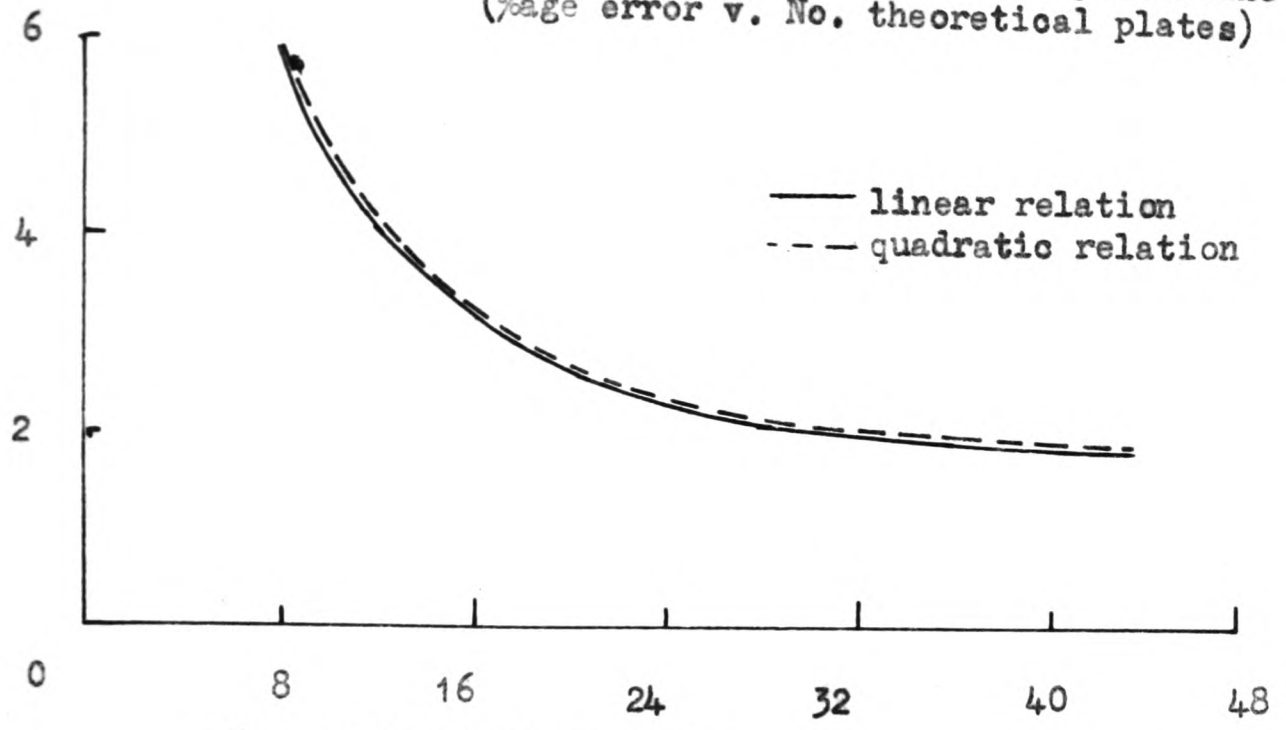
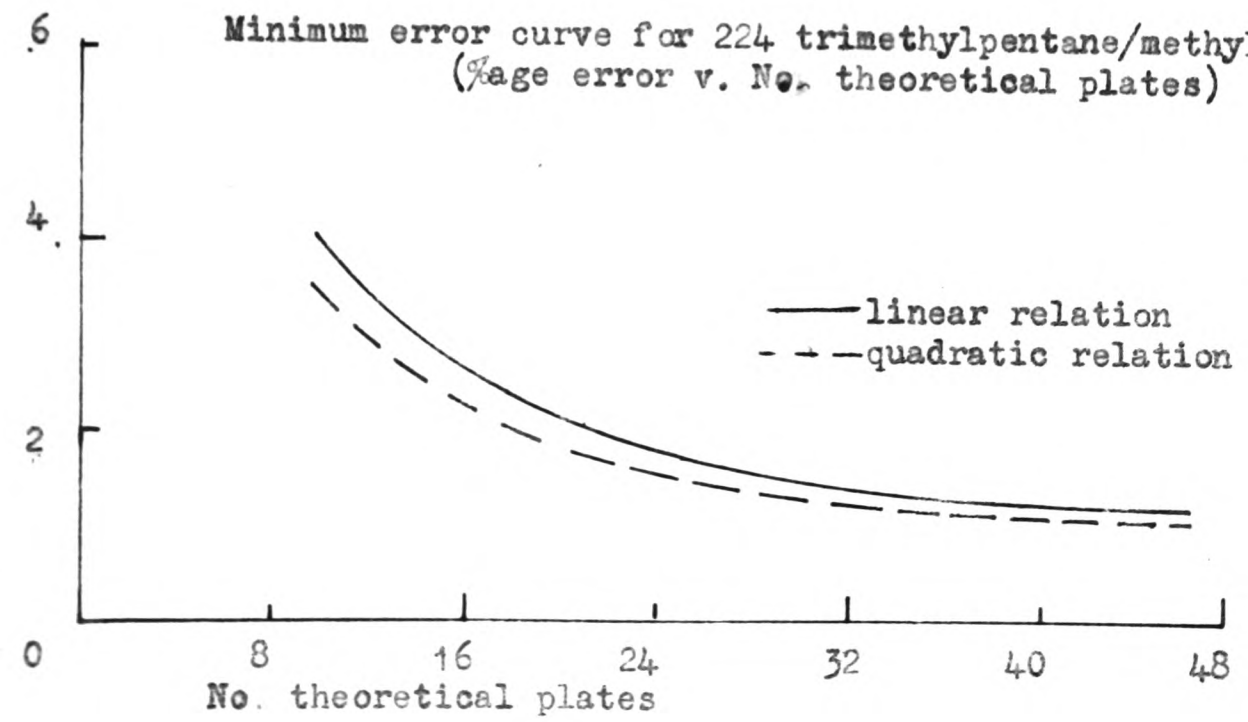


FIG. 3.2

Minimum error curve for 224 trimethylpentane/methylcyclohexane
(%age error v. No. theoretical plates)



Values of minimum percentage error have been plotted against the number of theoretical plates for the text-mixtures n-heptane-methylcyclohexane and 2,2,4 trimethylpentane-methylcyclohexane in Figs. (3.1) and (3.2). The errors are calculated using both the linear relation and the more correct quadratic relation. It is interesting to note that for the former test mixture, no difference results from using the linear relation, while for the 2.2.4 trimethylpentane-methylcyclohexane system, the errors calculated using the (more correct) quadratic relation are less than the corresponding values resulting from the use of the (incorrect) linear relation. The variation of minimum error on number of theoretical plates is therefore peculiar to each particular mixture. For the mixture n-heptane-methylcyclohexane, an error $\delta p = 1.5 \times 10^{-4}$ is assumed while for the other mixture under consideration 2.2.4 trimethylpentane-methylcyclohexane, the error $\delta p = .75 \times 10^{-4}$ is used. This is because the normal Abbé instrument is usually used for the former mixture, while the more accurate drum-reading Abbé refractometer is used for the latter, because the refractive indices of the components lie closer together therefore greater accuracy is required.

If the column to be tested has a small number of plates, it can be seen intuitively and by reference to Figs. (3.1) and (3.2) that it is advisable to use a test mixture whose relative volatility is higher, thereby increasing the difference between the stillpot and distillate concentrations, so reducing the error. The graphs show that the minimum percentage error rises more steeply as the number of plates is reduced below the optimum than on the high side of this point. Taking an arbitrary maximum value of 3%, the

n-heptane-methylcyclohexane mixture should not be used when N falls below 17, and the closer-boiling 2,2,4 trimethylpentane-methylcyclohexane should not be used when the column has less than 12 plates.

It thus appears that the former mixture, n-heptane-methylcyclohexane is suitable for columns with 17-50 plates, and the latter mixture is suitable for columns with 12-70 plates, using the appropriate refractometers.

Close examination of Figs. (3.1) and (3.2) reveals t that the n-heptane-methylcyclohexane and 2,2,4 trimethylpentane-methylcyclohexane curves have very shallow minima at N = 42 and N = 65 respectively. This was confirmed by derivation of an analytical expression for the percentage error, E. The number of plates, N, was then taken to be an independent variable (and not as a quantity which was given fixed discrete values as in the calculation of the graphical values), then the function was differentiated partially with respect to x_s and x_d . These simultaneous equations:

$$\frac{\partial E}{\partial x_s} = 0$$

$$\frac{\partial E}{\partial x_d} = 0$$

were then solved, and the values $x_s = 0.155$, $x_d = 0.806$ were obtained for the n-heptane mixture which resulted in a value of N = 42 when substituted in the Fenske equation.

Similar calculation for the 2,2,4 trimethylpentane mixture gave the values $x_s = 0.149$, $x_d = 0.793$ and N = 65.

A complete analysis of this problem is given in Appendix B.

3.2. Mixtures suitable for columns of high separating power

Physical properties.

Mention has already been made of two mixtures which are used for investigating the performance of high-efficiency separating columns. One mixture, n-heptane-methylcyclohexane has been widely used and has been the subject of many equilibrium determinations. Unfortunately, there still remains uncertainty about the ideality and relative volatility of this mixture, although in other respects the components satisfy the necessary criteria for a suitable text mixture having similar chemical and physical properties and vapour pressure ratios which vary by only a small amount over the concentration range. A table of the relevant physical properties of n-heptane, methylcyclohexane and 2,2,4 trimethyl-pentane is given below:

Table 3.1

		n-heptane	methyl cyclo hexane	2,2,4 T.M.P.
Boiling Point (°C)		98.427	100.934	99.238
Vap pressure (mm Hg)	at 98.427°C	760.00	707.880	747.710
	100.934°C	817.589	760.00	797.140
	99.238°C	778.270	724.458	760.00
η_L (centipoises)	at 100°C	0.208	0.30	-
ρ_L	at 100°C	0.6110	0.6992	0.6219
ν_L	at 100°C	0.341	0.43	
ν_v (224 TMP-MCH)	"	0·0306 cm²/sec		
D_v (n-heptane-MCH)		0·031		
D_v (2,2,4 TMP-MCH)		0·029		
Sc (2,2,4 TMP-MCH)		1·054		
Surface tension at 90°C		13.6	15	12.7
ΔH_v at B.P.		7.575	7.58	7.41
	n_D^{20}	1.38764	1.42312	1.39145
	n_D^{35}	1.38511	1.42058	1.38901

FIG.3.3(i).

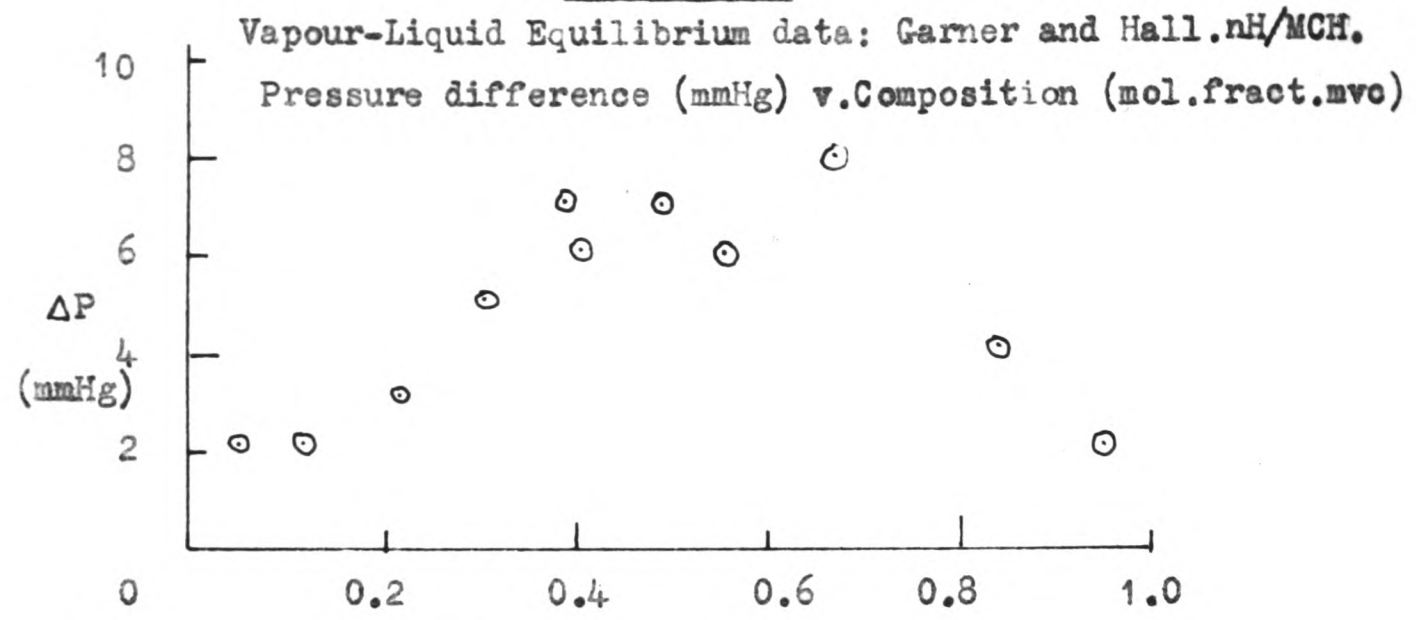
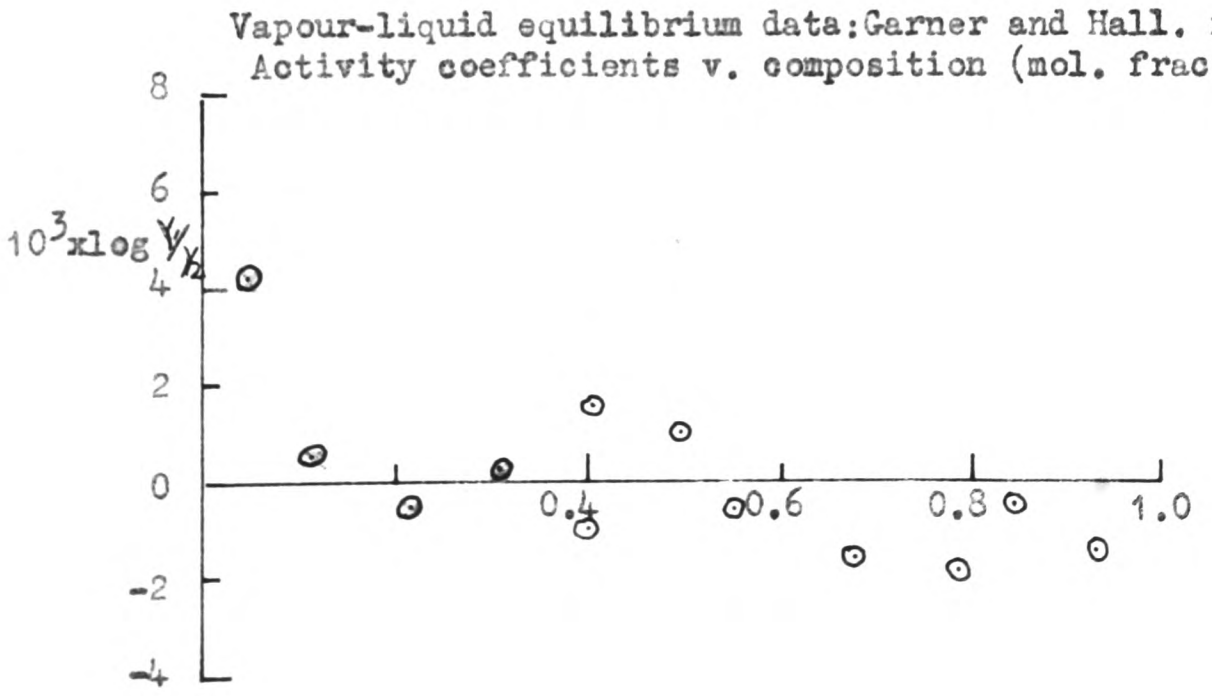


FIG.3.4(i).



All these values, unless otherwise stated, were obtained from the American Petroleum Institute Project No. 44 (32). Values of vapour kinematic viscosity were obtained from pressure drop measurements, the diffusivity values were evaluated from a modified correlation of Chapman and Cowling given by Chen (77) and the surface tension of methylcyclohexane was given by Zuiderweg (51).

3.2.1. Survey of atmospheric pressure data.
n-Heptane/Methylcyclohexane.
Total pressure data.

Bromiley and Quiggle (33) were among the earliest workers to investigate this system. They measured various physical properties of certain binary systems and also determined their vapour-liquid equilibrium data. The temperature-composition data for n-heptane-methylcyclohexane have been used to calculate the vapour pressures of the pure components from which the total theoretical pressures have been calculated using equation (3.4). Their total pressure data shows the system to be slightly non-ideal as the total pressure shows a slight dip in the mid-concentration region. Very similar results were obtained by Garner and Hall (34), but data obtained by Sieg (35) shows the system to be nearly ideal. These three sets of results are shown graphically in Fig. 3.3. (i), (ii) and (iii).

3.2.2. Vapour.liquid equilibrium data. Thermodynamic testing

The vapour liquid equilibrium data of Bromiley and Quiggle results in an average value of relative volatility $\alpha = 1.083$. However, a plot of log γ_1/γ_2 , the ratio of the calculated activity coefficients, against x, the mole fraction, shows the data to contain systematic experimental

FIG.3.3 (ii)

Vapour-liquid equilibrium data: Sieg. nH/MCH.

Pressure difference (mmHg) v. composition (mol.fract.mvc)

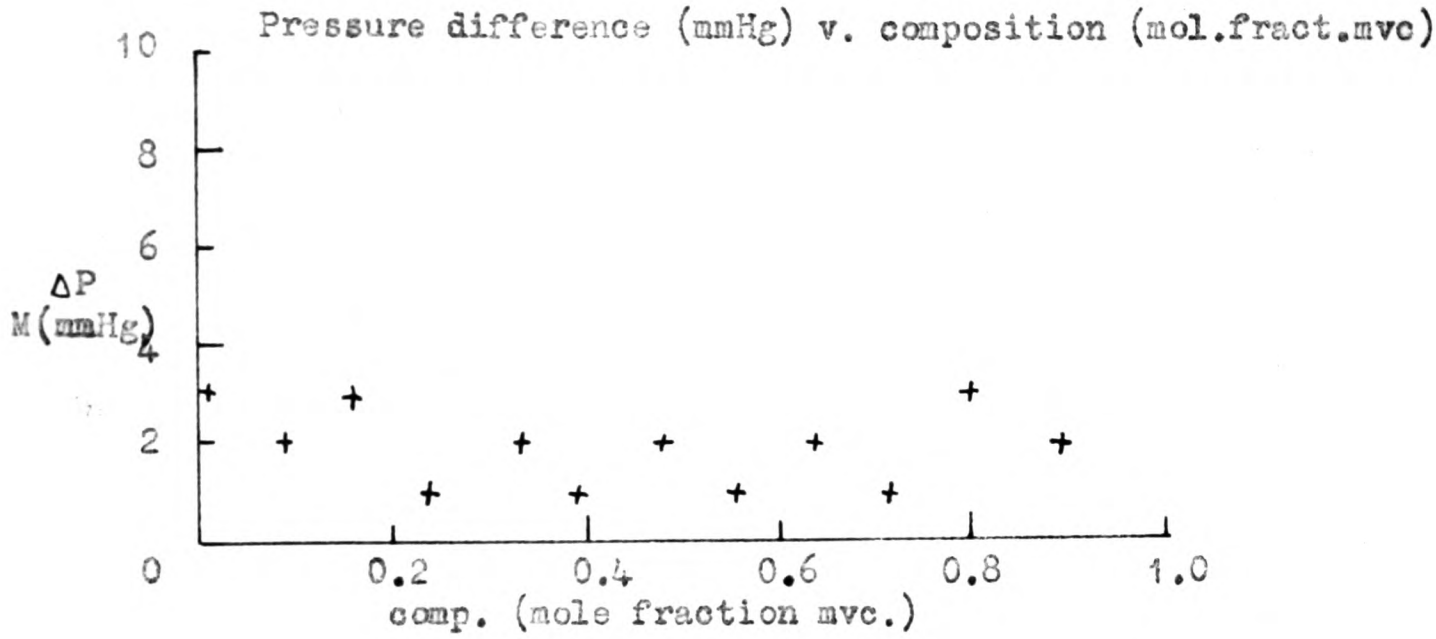
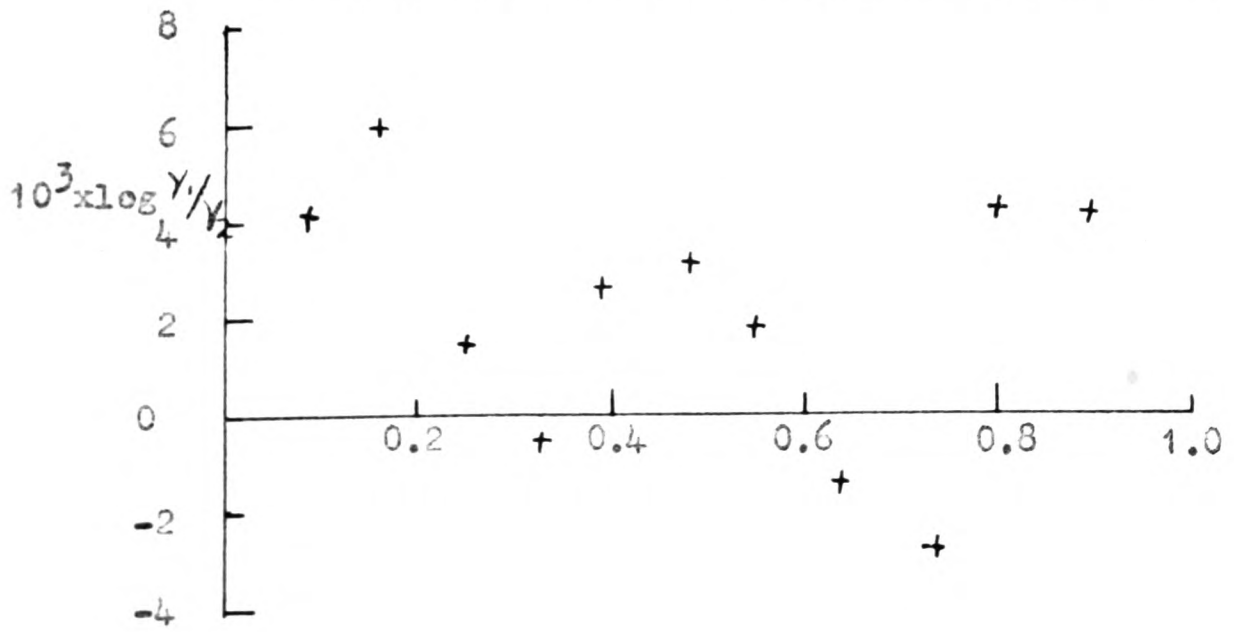


FIG.3.4 (ii)

Vapour-liquid equilibrium data: Sieg. nH/MCH.

Activity coefficient v. composition (mol. fract.mvc).



errors, and the results to be thermodynamically inconsistent. This plot and those drawn from other vapour-liquid equilibrium studies are shown in Fig. 3.4.

The activity coefficients, γ_1 and γ_2 were calculated from equation (3.7) and the gas deviation factors, Z_i, from (3.8). Values of the second virial coefficients B for n-heptane-methylcyclohexane and 2,2,4 trimethylpentane were determined from critical data for the three compounds using a method due to Black (36). Critical data for two of the substances were obtained from the literature (32), but values for methylcyclohexane were estimated using a correlation of Stiel and Thodos (37). Relevant values are given below:

	n-heptane	methylcyclohexane	2,2,4 T.M.P.
T_c (^oK)	540.16	569	544.31
P_c (atmos.)	27.01	60	25.30
B	- 1264	- 910	- 1374
Z_1 at 98.5	1.000	0.998	0.999
Z_1 at 99.1	1.001	0.998	1.000
Z_1 at 100.0	1.002	0.999	1.001
Z_1 at 101.0	1.004	1.000	1.002

Van Wijk and Thijssen (38) have also checked the data of Bromiley and Quiggle, and found them inconsistent. Accordingly, they had the system redetermined, and found it to be ideal, obeying Raoult's Law. They recommended a value of $\alpha = 1.075$.

Identical thermodynamic tests were applied to the data of Garner and Hall and of Sieg. As Sieg's data showed a scatter, it was not possible to apply the test rigorously. An average value of $\alpha = 1.075$ was obtained. The data of Garner and Hall appeared consistent and the relative

FIG.3.3 (iii)

Vapour-liquid equilibrium data: Bromiley. nH/MCH.

Pressure difference (mmHg) v. composition (mol.fract.mvc)

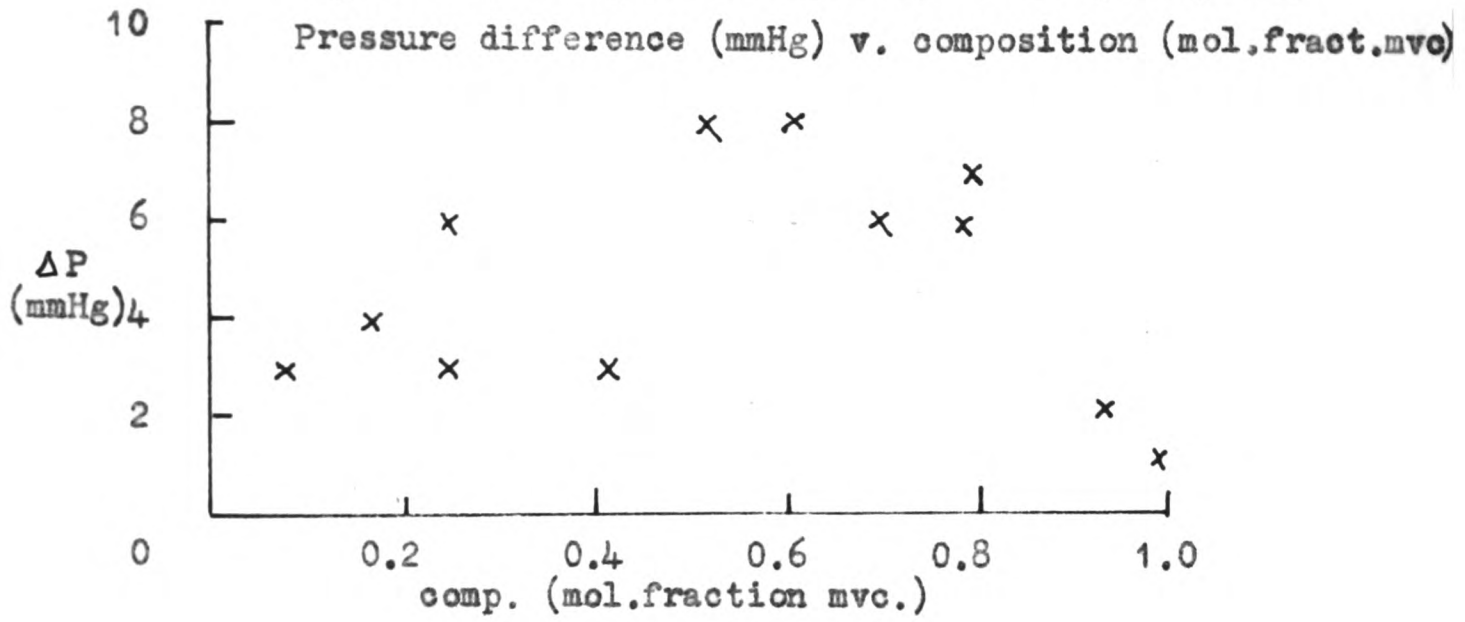
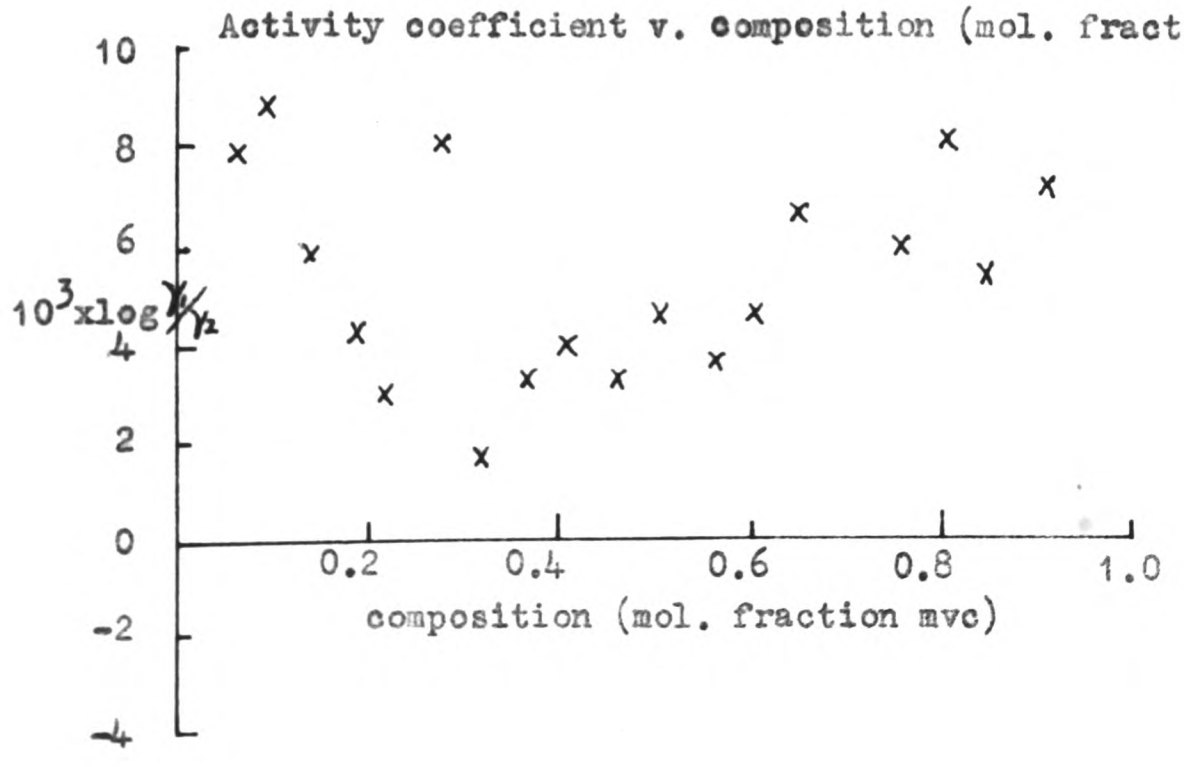


FIG.3.4 (iii)

Vapour-liquid equilibrium data: Bromiley. nH/MCH.

Activity coefficient v. composition (mol. fract. mvc)



volatility was seen to fall from a value of 1.073 through a mid-value of 1.070 to a low of 1.067. Since this fall is very slightly greater than the slight decrease in α obtained from vapour pressure ratios and the calculated total pressure showed a slight dip in the mid-concentration range, They concluded that the mixture was nearly ideal.

Working soon after Bromiley and Quiggle, Beatty and Calingaert (39) conducted a series of total pressure measurements on six binary systems, including n-heptane-methylcyclohexane. With this system, they found no variation in the total pressure over the concentration range, and concluded that the system was ideal with a relative volatility of $\alpha = 1.07$. Griswold (40) pointed out that a constant total pressure did not necessarily indicate ideality, then showed the relative volatility to be 1.083. This result was obtained by distilling the test mixture in a packed column. As the number of plates in the column had been previously determined by distilling a benzene-carbon tetrachloride mixture of known relative volatility, the correct value of α could be calculated from the amount of n-heptane present in the stillpot and distillate samples using Fenske's equation. This value was supported by comparison with the Bromiley and Quiggle value. Since different test mixtures used in the same column under identical operating conditions do not necessarily give the same number of theoretical plates, and the Bromiley and Quiggle data have been shown inconsistent, it is difficult to admit this value as satisfactory.

As there are different values of relative volatility quoted for this mixture, care must be taken when comparison is made between the results of various workers. Shahbenderian (3) Burk et al. (41) Lecky and Ewell (42) all use the value of α = 1.07 obtained by Beatty and Calingaert. Lecky and Ewell also constructed a curve of refractive index against number of plates, which others used. Willingham et al. (43) assumed the mixture to be ideal, while Griswold (40) Matterson (1) and Sladacek used α = 1.083.

Recent vapour pressure measurements (32) give the vapour pressure ratios varying from α = 1.0736 to α = 1.0758; the mean value is α = 1.075.

3.2.3. 224-Trimethylpentane/methylcyclohexane.

Another system which is suitable for evaluating columns of high separating power is 2,2,4 trimethylpentane-methylcyclohexane. The physical properties of the iso-octane are given in Table 3.1 along with those of n-heptane and methylcyclohexane, and comparison of the respective properties of the components comprising this binary mixture shows them to be similar. The vapour pressure ratios appear to vary considerably less than do those for the n-heptane-methylcyclohexane system, but unfortunately the refractive indices lie closer together. This necessitates the use of a Pulfrich or drum-reading Abbé refractometer to achieve the desired accuracy.

Three sets of vapour-liquid equilibrium data have been determined for this system. The data of Harrison and Berg (44) show so much scatter that no satisfactory conclusion may be drawn as to an appropriate value of α, and neither is it possible to determine whether the system is ideal.

FIG.3.5

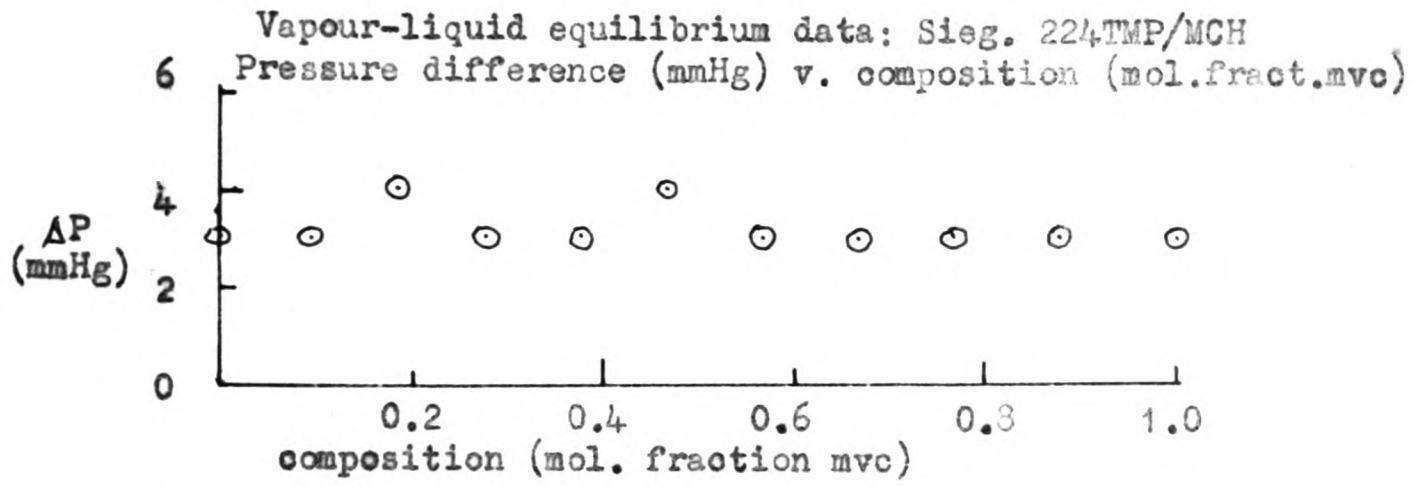
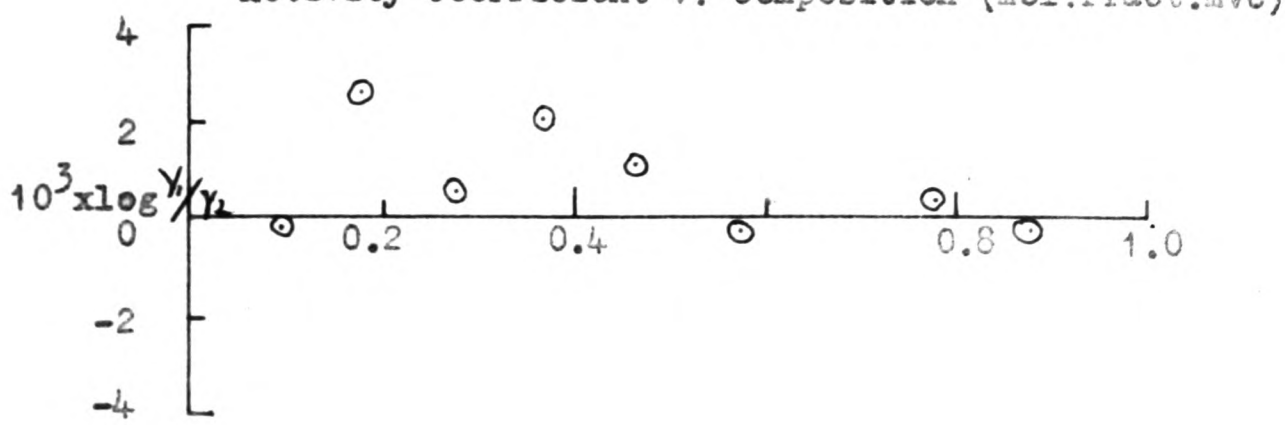

Vapour-liquid equilibrium data: Sieg. 224TMP/MCH
Pressure difference (mmHg) v. composition (mol.fract.mvc)
ΔP (mmHg)
6
4
2
0
0.2
0.4
0.6
0.8
1.0
composition (mol. fraction mvc)

FIG.3.6


Vapour-liquid equilibrium data: Sieg. 224TMP/MCH
Activity coefficient v. composition (mol.fract.mvc)
$10^3 x \log \gamma_1/\gamma_2$
4
2
0
-2
-4
0.2
0.4
0.8
1.0

The total pressure figures calculated from the data of Sieg (35) show a negligible variation over the concentration range, but they are all about 3 mm. below the measured atmospheric pressure of 760 mm. This suggests that either the value of 760 mm. is in error, or the data were subject to systematic error. Gelus, Marple and Miller (45) obtained data which showed a slight fall around the mid-concentration values. This indicated the mixture to be very slightly non-ideal. Unfortunately, their vapour-liquid equilibrium data were not amenable to thermodynamic testing due to experimental scatter, but the data of Sieg appear to be thermodynamically consistent, and give an average value of $\alpha = 1.049$, which agrees with the vapour pressure value given above. The total pressure data and plot of the ratio of activity coefficients of against mole fraction of Sieg are shown in Figs. 3.5 and 3.6 respectively.

3.3.1. Survey of sub-atmospheric pressure data

Bragg and Richards (46) have suggested benzene-ethylene dichloride as suitable for work at moderate vacuum in the pressure range 100 mm. - 400 mm. Hg, and at lower pressures of 50 mm - 10 mm. they recommended the use of o-dichlorobenzene-p-diethylbenzene. However, even at the highest operating pressure of 400 mm. the boiling points are 60.6°C for benzene and 83.7 °C for ethylene dichloride respectively, both of which are well below the recommended minimum value. Moreover, the vapour-liquid equilibrium data for both systems show large-experimental errors, so it is not possible to apply a thermodynamic test for consistency. Bliss, Eshaya, and Frisch (47) also tested the o-dichlorobenzene-p-diethylbenzene system at pressures of 100 mm. 50 mm and 10 mm Hg.

Their results show much less scatter than do those of Bragg and Richards. In addition, they also measured the vapour pressures of the pure components, expressing the results in a form of relation similar to the Antoine equation. A thermodynamic check on the data obtained at 50 mm. Hg unfortunately shows these to be inconsistent and the mixture to be non-ideal. Feldman et al. (48) investigated two mixtures for moderate vacuum work. Dodecane-cyclohexylcyclopentane has a relative volatility which varies from 1.13 - 1.18 at a pressure of 100 mm., while the second mixture, n-tridecane-dicyclohexyl forms an azeotrope at 75% mole fraction of one component. No vapour pressure data were presented for these compounds and so thermodynamic testing is not possible.

Feldman (49) in a study of separation of 1 and 2 methyl naphthalenes by azeotropic distillation using undecanol suggested that the mixture of monomethylnaphthalenes to be suitable for testing high performance columns under vacuum. At the lowest pressure of 20 mm. Hg. the mixture will boil about 125°C rising to a value of 180°C at 150 mm. Hg. This latter value is too high for convenient testing. He observed that reliable vapour-liquid equilibrium measurements on systems having low vapour pressures are difficult to make the experimental error being sometimes greater than the change in composition, and used a packed column of known separating power in a manner similar to Griswold. Values of α so obtained ranged from 1.10 to 1.05 at 20 mm. pressure and from 1.11 to 1.07 at 150 mm. pressure. As Griswold's data for the n-heptane methylcyclohexane system at atmospheric pressure have been shown to be of doubtful value, and a change of 1.10 to 1.05 results in a very large change in the number of plates

calculated by the Fenske equation, it is likely that Feldman's recommended values of 1.07 or 1.11 are of little use. It is unfortunate that he conducted no vapour-liquid equilibrium studies on the monomethylnaphthalene system, as the binary systems with undecanol were investigated and the data thermodynamically checked.

The two systems suggested by Berg and Popovac (50), n-heptane-toluene and n-heptane-n-octane appear completely unsuited to vacuum work. At 400 mm. Hg. pressure, n-heptane boils at 78°C rendering the former system unsuitable, and the relative volatilities vary considerably over the concentration range. Also then experimental vapour-liquid equilibrium measurements show a considerable scatter.

3.3.1.1. Use of n-decane/transdecalin.

The system n-decane-transdecalin has been subject to three investigations. From consideration of boiling-point, this system is well suited to evaluating distillation columns under pressures 50 - 200 mm. Hg., the boiling-point varying from $\sim 95^{\circ}C$ at 50 mm. Hg. to $\sim 130^{\circ}C$ at the higher pressure. Remaining physical properties are given in the following table:

Table 3.2

		50% mole mixture
Boiling point(°C)		111.9
η_L	(centipoise)	0.56×10^{-2}
η_v	"	6×10^{-5}
ρ_L	(gm/ml)	0.77
ρ_v	"	0.6×10^{-3}
ν_L		0.73×10^{-2}
ν_v		1×10^{-3}
$\mathcal{D}_v$		19×10^{-2}
$\mathcal{D}_L$		1.5×10^{-5}
Sc_v		0.53
Sc_L		500
	n-decane	transdecalin
n_D^{25}	1.40967	1.4672
n_D^{20}	1.41189	1.4695

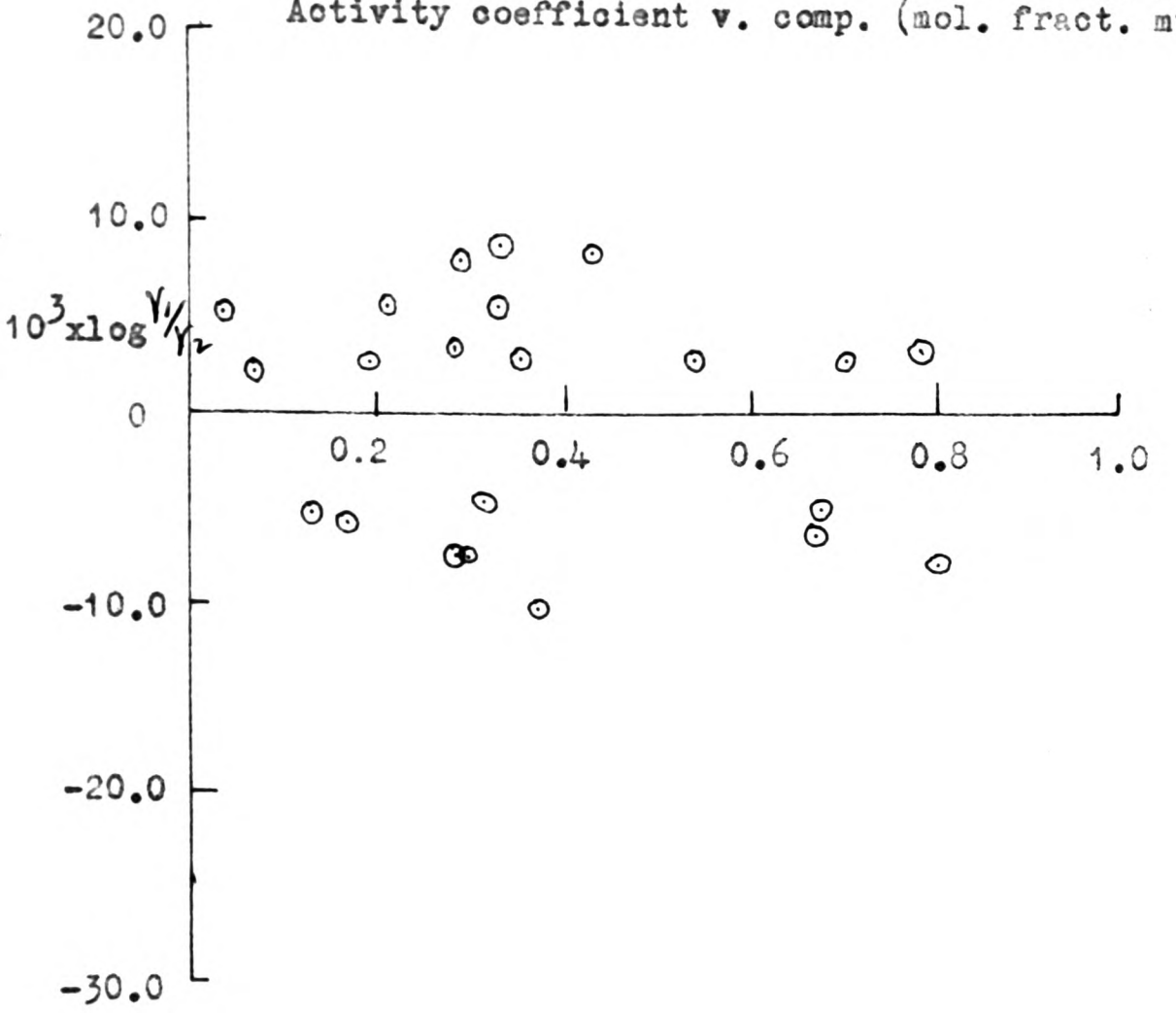
Apart from the values of refractive index which are given by the A.P.I. Research Project (32), the values in the above table are given by Zuiderweg (51). All figures are for the operating pressure of 100 mm. Hg. Values at other pressures are also given by Zuiderweg in the same paper.

3.3.1.2 Thermodynamic testing of n-decane/transdecalin.

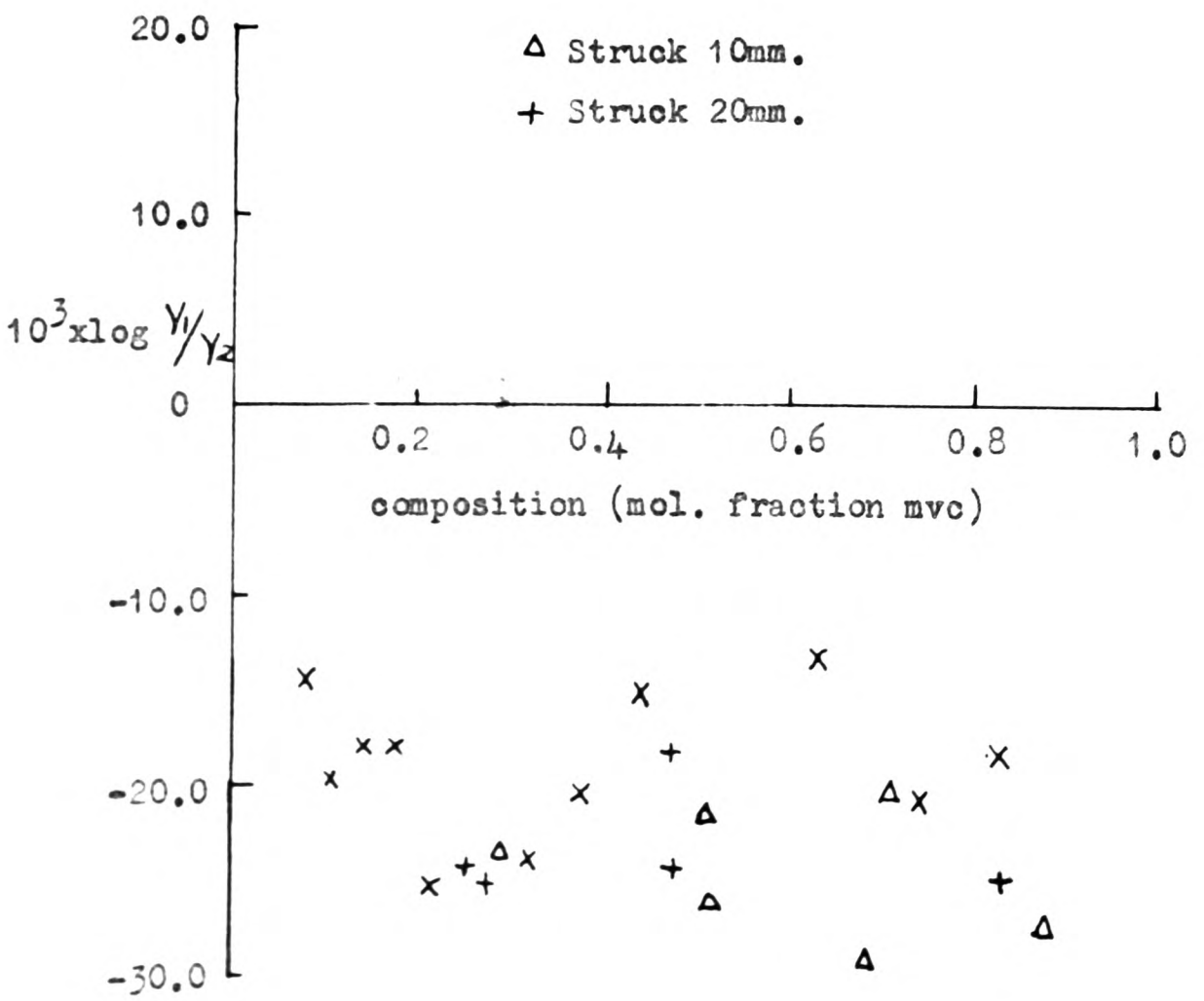
Fenske, Myers and Quiggle (52) determined vapour-liquid equilibrium data using an Othmer-type still of two theoretical plates. They obtained relative volatility values over the concentration range at pressures of 740 mm., 200 mm. and 50 mm. Hg. As the relative volatility values were constant at each of these pressures, single values were obtained for numerous intermediate pressures. Good agreement

FIG.3.7 (i)

Vapour-liquid equilibrium data: Zuiderweg. n-Decane/transdecalin.
Activity coefficient v. comp. (mol. fract. mvc)



Vapour-liquid equilibrium data. n-Decane/transdecalin
Activity coefficient v. composition (mol. fract. mvc)
× Fenske 760mm.



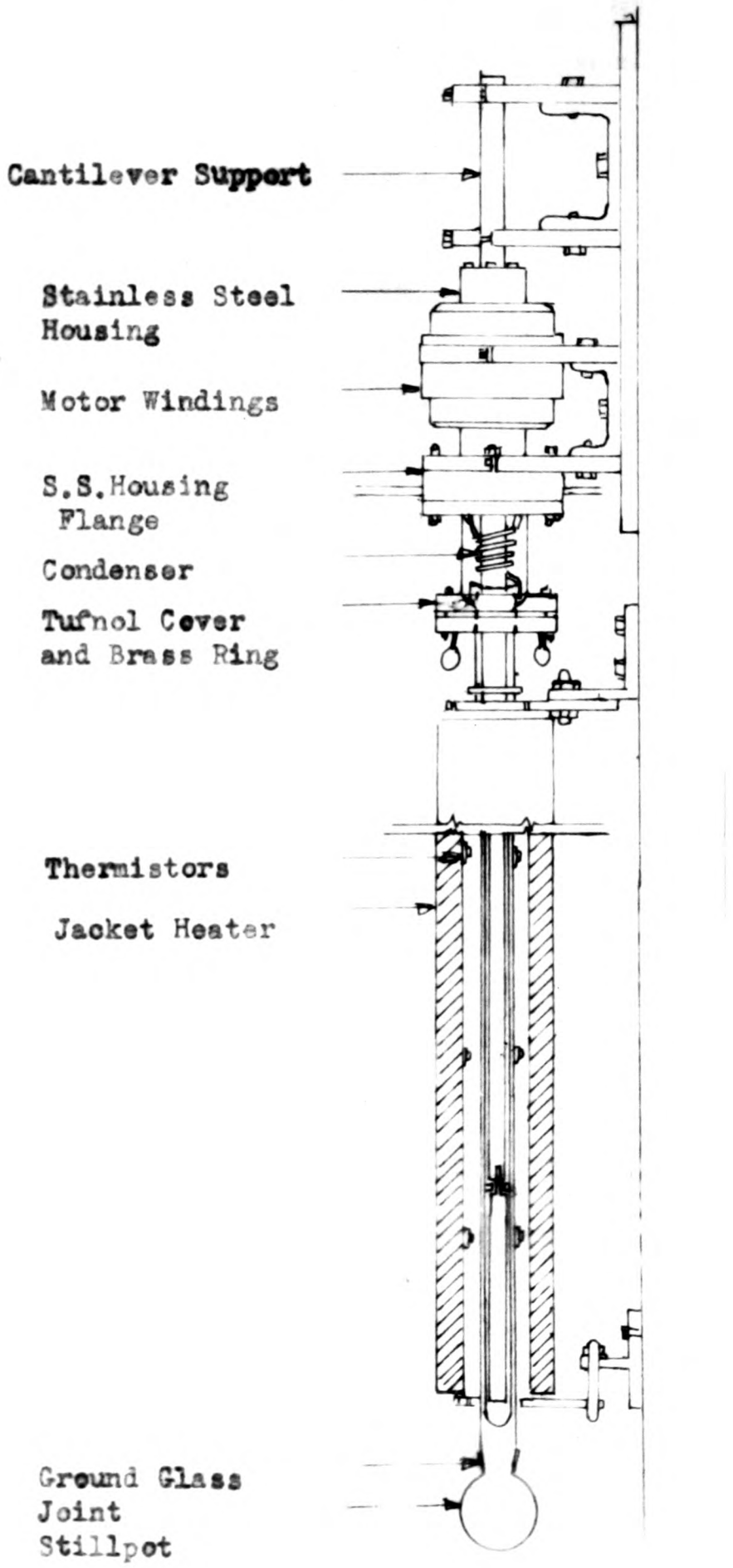
was obtained with the data of Struck and Kinney (53), who used a single-plate Othmer still. They also determined relative volatilities at pressures of 20 mm. and 10 mm. As neither sets of data had any thermodynamic test applied, any possible systematic errors remained undetected.

Zuiderweg (51), in addition to examining the vapour-liquid equilibrium data at atmospheric pressure, measured the vapour pressures of the pure components at various temperatures. He then calculated the activity coefficients γ_1 and γ_2 and by applying the equal areas criterion with equation (3.10) showed the system to be ideal with a constant relative volatility and his data to be thermodynamically consistent. Accordingly only a few check determinations were performed at reduced pressure, since the vapour pressures can be used to calculate the required relative volatility values. In addition, the ideality of the mixture was confirmed by a comparison of the measured total pressure of a 50% mole mixture with the calculated total pressure using Raoult's Law. As the relative volatility values obtained from Fenske et al. and Struck et al. were significantly different, Zuiderweg compared their observed and calculated total pressures, and plotted log γ_1/γ_2 v x for their vapour-liquid equilibrium data. This showed that their data are thermodynamically inconsistent, and systematic errors were present. These three sets of results are shown in Figures 3.7 (i) and (ii).

n-Decane/transdecalin with the data of Zuiderweg is therefore recommended for testing fractionating columns under moderate vacuum.

FIG.4.1

Diagram of Column 1.



CHAPTER IV

4.1. Column.1.

4.1.1. Introduction and General Description of column 1.

Column 1 was, apart from slight modifications, the same as the column 2 described by Macleod and Matterson (2) and the distillation column used by Shahbenderian (3). It is shown diagrammatically in Fig. 4.1.

The rectifying section consisted of a vertical hollow aluminium rotor with an external diameter of 2.2 cm., surrounded by a glass stator of 2.8 cm. internal diameter; this gave an annular clearance of 0.3 cm. The rotor was closed at the lower end, and could be driven by means of a 1/25 H.P. squirrel cage induction motor coupled to the upper end. Originally, the length of this rectifying section was 61 cm.; this was later shortened to 59 cm. The complete rotor assembly was supported by means of a silver steel cantilever, which was firmly held at its upper end by two Vee blocks mounted on a massive piece of channel.

The motor rotor was surrounded by a housing made of thin gauge stainless steel. This housing was connected to the column by means of a system of flanges and 'O' rings, thus ensuring the whole column was gas-tight. This was intended to allow for vacuum operation without the need for a rotating mechanical shaft seal.

The vapour ascended from the boiler along the annular gap and was condensed immediately above the stator upon a double-wound copper condenser coil. The liquid reflux was then returned to the stator by means of a weir whose purpose was to ensure uniform reflux distribution. This weir and condenser arrangement, described in more detail below constituted the principal improvements in this apparatus over

that of Shahbenderian. The stillpot consisted of a 500 ml. 3-necked round-bottomed flask, which had provision for thermocouple entry. The third opening was connected with a three-way stopcock and hypodermic syringe so that samples from the stillpot could be withdrawn. Distillate samples were removed through two stainless steel needle valves with P.T.F.E. seats, connected to the underside of the weir. Boilup rate measurements were made by means of a glass trap and side-arm described by Matterson. This boilup meter was interposed between the stillpot and lower end of the stator. Power was supplied to the stillpot by means of a 500 watt isomantle heater using a 'Variac' variable transformer, and operating conditions were maintained as nearly adiabatic as possible by means of automatically controlled jacket heaters.

4.1.2. Description, Modification and Operation of Rotor Assembly.

The rotating member of the column consisted of a hollow cylinder of aluminium which was closed at the lower end and flexibly coupled at the upper end to the rotor of a 1/25 H.P. squirrel-cage induction motor.

The variable frequency speed control consisted of a 1/4 H.P. induction motor which drove a rotary converter through a Kopp variable speed gear. The D.C. brushes of the converter had been removed, so that an alternating current, whose frequency was dependent on the converter shaft speed, was obtained. This A.C. output was connected to the stator windings of a 2 pole 1/25 H.P. squirrel cage induction motor, which, when connected to 50 c/s A.C. gave a speed of 2850 r.p.m.

By altering the output speed of the Kopp variator, rotor speeds from 300 r.p.m. to 2,500 r.p.m. could be obtained. When the squirrel-cage stator winding was directly connected to the mains to give a speed of 2,850 r.p.m., a 5 μF condenser and discharge resistance were connected across the starter coil in order to provide an out-of-phase current for starting the motor. When, however, the motor was operated using the variable frequency generator a capacitance of 10 μF was used. For low-speed operation, it was necessary to increase this value to 19 μF by switching in a further 9 μF in parallel, otherwise the rotor motion became irregular.

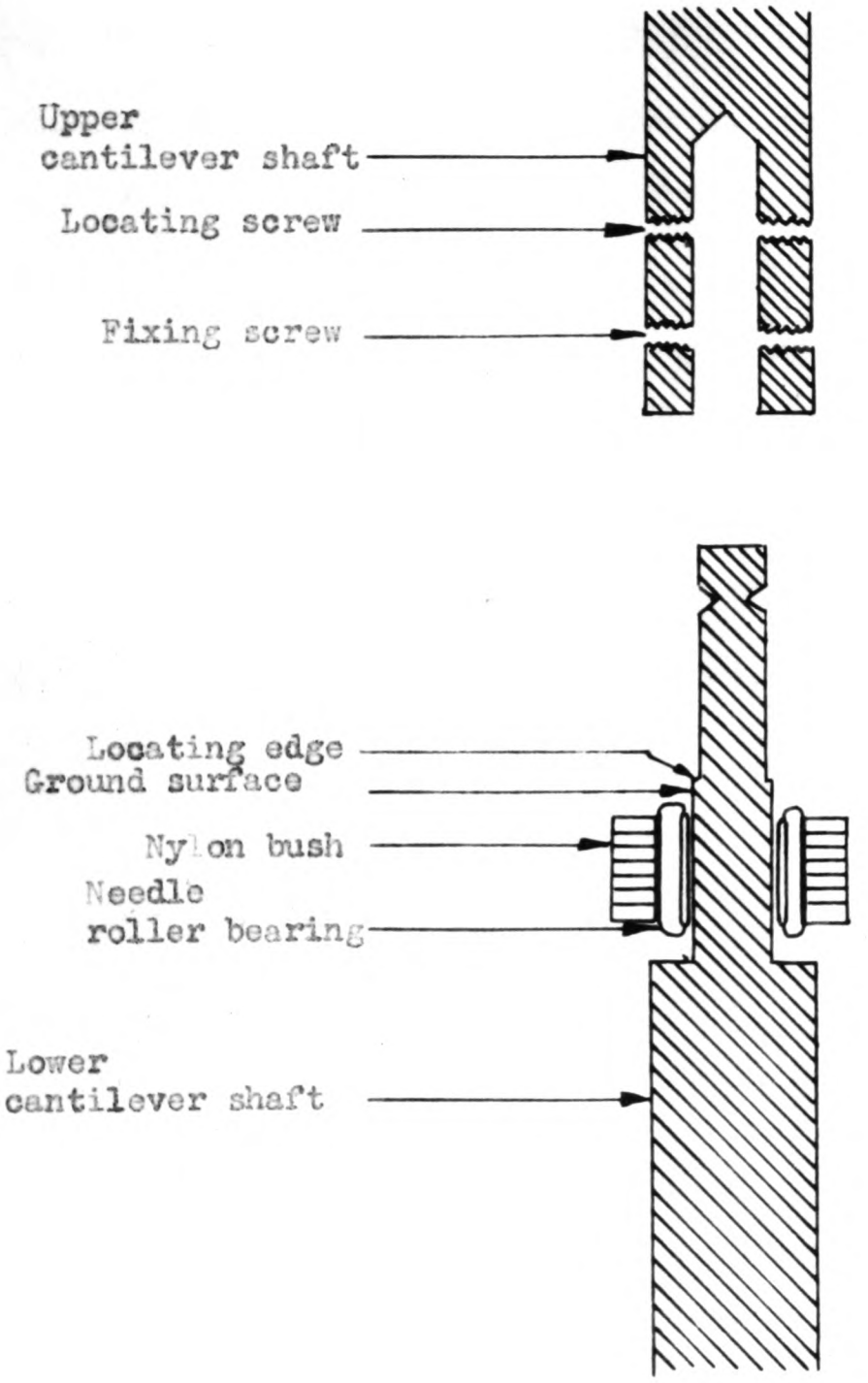
The lower bearing was so placed that the rotor length above the bearing was two to three times the length below. The rotor bearings were supported by a 3/4" diameter silver steel cantilever securely fixed at the upper end as explained above, and extending some distance below the lower bearing at its free end.

4.1.2.1. Modifications

Extensive experiments by Macleod and Matterson showed that as the rotor speed is increased, the support system passes through one or more critical speeds. Above the uppermost critical speed the rotor should run without perceptible vibration. The principal advantage of such a 'loaded-cantilever' system for use in a distillation column is that there are no bearings exposed to hydrocarbon vapours, while the use of a 'canned' motor eliminates the need for a rotating mechanical shaft seal even when the system is operated under sub-atmospheric conditions. Mechanical troubles have been

FIG.4.2

Column 1. Detail of lower bearing assembly.



reported (54) with systems where the bearings were exposed to hot hydrocarbon vapours.

The cantilever system as originally designed, was found to be mechanically unsatisfactory because of the small diameter and lack of stiffness of the intermediate portion carrying the lower bearing of the rotor. This lower bearing was originally an angular contact ball race; replacement by a needle roller bearing allowed the use of a larger diameter spindle connecting the upper and lower parts of the cantilever with consequent increase in rigidity. The needle rollers ran on the hardened and ground surface of the central spindle, which was integral with the lower part of the cantilever. The outer race of the bearing was pressed into a nylon collar. This collar had a thin circumferential lip machined around the outer surface to provide a sliding fit with the internal surface of the aluminium rotor. Details of the modified design is given by Fig.4.2.

Modified in this fashion, the whole cantilever system was found to be more rigid, and no independent oscillation of the detachable lower part occurred in use. Unfortunately, the self aligning characteristics of the angular contact bearing used by Matterson and Shahbenderian were lost by using the needle roller bearing. Considerable mechanical trouble was experienced: this took the form of small sustained oscillations at speeds other than the critical. Although such oscillations may not have been caused by the use of this bearing, it is thought likely that they would have been effectively damped had the angular contact bearing been used. Weight is added to this hypothesis by the fact

that use of the copper and glass rotors which had been used by the previous workers on this column, was not possible: the glass did not seem able to pass through the critical speed, while with the copper rotor, oscillations of such magnitude occurred at the critical speed that these were sustained by the striking of the rotor against the glass stator when that was in position, although they damped satisfactorily when the stator was not in position.

In all experimental runs with this column, the rotor was a thin-walled aluminium tube of 2.2 cm. external diameter and 61 cm. long. The upper critical speed was ~1,100 r.p.m. but sustained oscillation of the cantilever and rotor was observed at speeds between 800 r.p.m. and 1,300 r.p.m. This oscillation was greatest at 1,100 r.p.m. though when the rotor speed was maintained at 1,300 r.p.m. for periods of time exceeding ten minutes there could be observed slight oscillations which increased in amplitude. When the apparatus was at room temperature these oscillations were entirely absent at speeds up to 800 r.p.m. and from 1,300 r.p.m. to 2,400 r.p.m. It was also possible to run the rotor at 2,850 r.p.m. from the mains. When, however, the rotor was turned under distilling conditions, i.e. with the rotor hot, slight but prolonged oscillations were experienced at speeds which had formerly been trouble-free. After some time, this most undesirable characteristic was removed by stripping all the grease from the lower bearing and relubricating with 'Molyslip', a molybdenum disulphide suspension. Several months of trouble-free operation were then experienced.

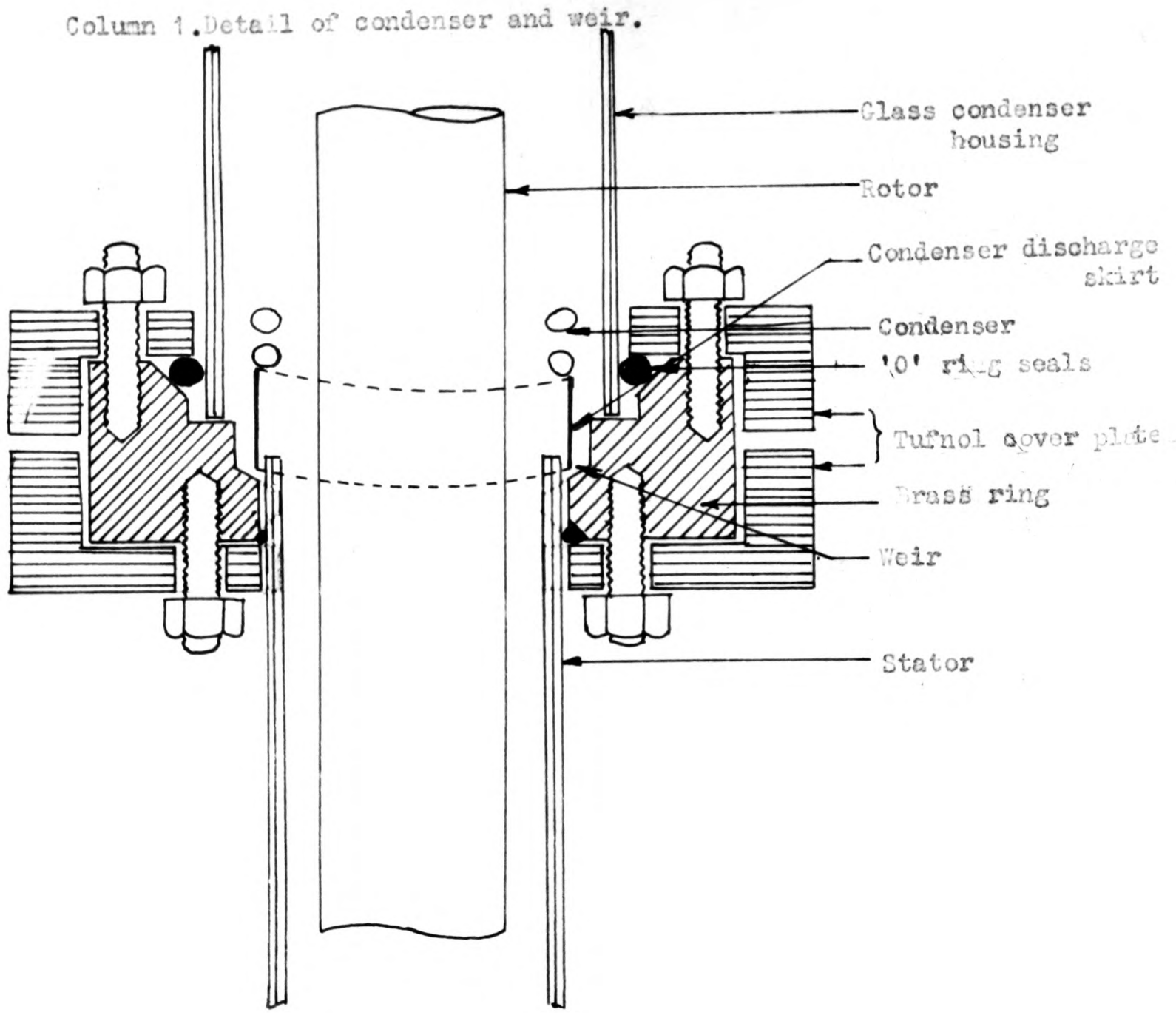
Unfortunately, similar trouble was again experienced when, due to a failure in the water coolant supply to the condenser, it became necessary to strip the colum completely and replace the motor rotor bearings. Various attempts were made to locate the source of the trouble, and although various alterations and slight improvements were made, the unstable rotor operation persisted. It was found that the trouble disappeared when the stator windings were energised direct from the mains, rather than from the rotary generator of the speed-control system. It was therefore decided to use the two available stator windings connected directly to the mains and run the column at the synchronous speeds of 1,470 r.p.m. and 2,850 r.p.m., at which no trouble was experienced; a pole winding was available for the lower speed. As it was still possible to use the rotary converter for the lowest speed of 670 r.p.m. a good range of speeds was available. When the stator windings were connected directly to the mains, the capacitance of the starter condenser was reduced to the recommended value of 5 μF.

Later, the trouble was largely cured by mechanical improvements in the motor-drive rotary generator system.

4.1.3. Condenser design

Shahbenderian had noted that when his distillation column was operated at low boilup rates and low speeds of rotation, abnormally high values of H.E.T.P. were obtained. This he attributed to the channelling of the reflux stream in the absence of a proper weir at the top of the column. Reflux distribution was supposed to be effected by a string wiper attached to the rotor, but Shahbenderian doubted the effectiveness of this device.

FIG.4.3


Column 1.Detail of condenser and weir.
Glass condenser housing
Rotor
Condenser discharge skirt
Condenser
'O' ring seals
Tufnol cover plate
Brass ring
Weir
Stator

The condenser assembly was redesigned as shown in Fig. 4.3 to try and eliminate this source of channelling, by improving the reflux distribution. The outer tube of the column was no longer made integral with the jacket of the condenser as before. Its upper edge was carefully ground flat and square to the axis in the lathe to form the overflow edge of the weir, while the liquid was retained by an annulus of triangular cross-section between the outer wall of the glass stator and a 45° chamfer machined in a surrounding brass ring. This ring was held in position by a system of O-rings and Tufnol flanges. Distillate could be removed from the column by means of two stainless steel needle valves with P.T.F.E. seats, each of which was connected to 2 holes leading from the weir to the underside of the brass ring. Visual observation of the reflux indicated that the reflux distribution was greatly improved by this arrangement.

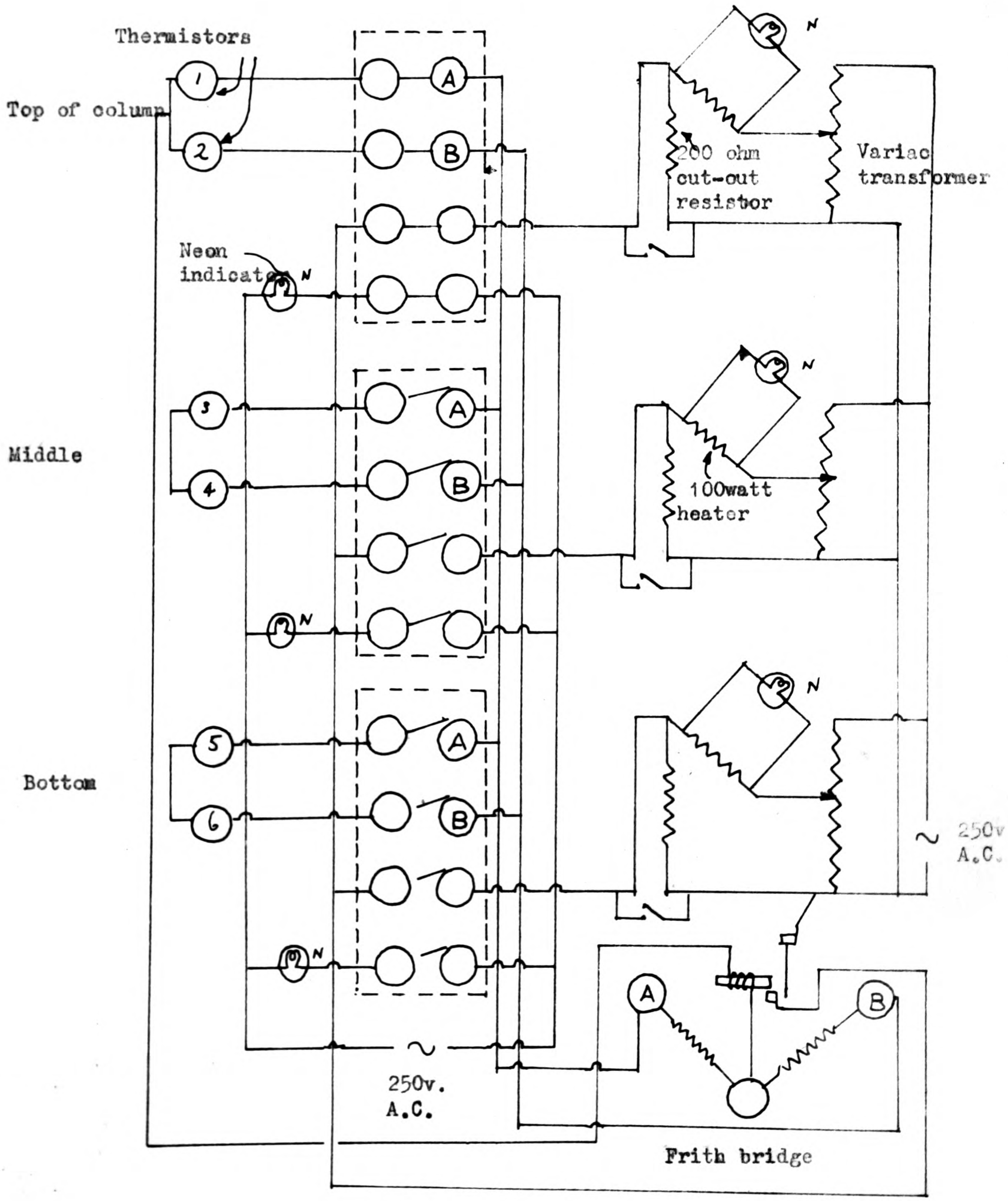
A double-wound countercurrent copper condenser coil which terminated at its lower end in a single copper ring had its inlet and outlet fitted through the existing aluminium support ring which was attached to the stainless steel housing surrounding the squirrel-cage motor. This copper ring had a narrow strip of perforated brass soldered to it, thereby enabling the condensate leaving the condenser to drain uniformly into the weir prior to returning to the column.

4.1.4. Adiabatic control.

The adiabatic control system was similar to that used by MacLeod and Matterson. The rectifying section of the column was supported by a tubular copper jacket, which was surrounded by a heating jacket wound in three sections;

FIG.4.4

Thermistor scanning assembly and Frith Bridge.



each section being rated at 100 watts. Power was supplied to each section by a variac through a 200 ohm series resistor. Corresponding with each section was a pair of matched thermistors: one on the column wall, the other on the copper jacket. Each pair could be connected to a Frith bridge by a rotary switch which made a complete revolution every minute. When a radial temperature gradient existed the difference in resistance between the thermistors connected to the bridge caused a relay to close a switch wired in parallel with the 200 ohm series resistor, thereby increasing the heating current in the particular section of the heating jacket. The system is shown diagrammatically in Fig. 4.4

One thermistor of each pair was wired in series with a wirewound 100 ohm trimmer. Thermocouples mounted alongside the thermistors enabled the absolute and differential temperatures in the column to be measured. To ensure a balance between each thermistor pair, the column was switched on, and, when the radial temperature gradients as measured by the thermocouple pairs become zero, and the wall temperatures reached the boiling point of the test mixture, the slide-wire of the Frith bridge and the thermistor trimmers were adjusted so that the bridge relay had just switched off, thereby reducing the power input to each section. The variac settings were chosen so that when the relay was open the power supplied was insufficient to maintain the wall temperature at the required value, and when the relay was closed, the full power supplied was greater than that necessary to maintain the correct wall temperature. As it was not found possible to obtain a balance with an air gap, the space between the column and the tubular jacket was filled with asbestos

string thereby preventing radiant heat transfer and air circulation between the wall and jacket thermocouples and thermistors.

4.1.5. Other miscellaneous improvements.

When the column was taken over from Shahbenderian, the electrical system was completely rewired, and the existing heating jacket was replaced by one which was commercially made. Other slight modifications were also made. In an attempt to reduce the variability of heat losses from the stillpot, an aluminium windshield was placed around it. Later, the power to the stillpot heater variac was supplied through a constant-voltage transformer, so that fluctuations due to mains voltage variations were eliminated. Heating tapes were wound around the exposed portion of column immediately below the condenser weir, and around the boilup meter.

In addition the glass tap and barrel of the boilup meter were replaced by a 3 mm. stopcock made of P.T.F.E. which turned in a glass barrel of appropriate size. As P.T.F.E. is self-lubricating, grease which formerly had been required was no longer needed, and there was no consequent contamination of the test mixture which had acted as an efficient degreasing material for the lubricated stopcocks formerly used.

All the ground glass joints had been sealed with Audco valve lubricant. Although this was a most effective sealer, it caked hard after a short period of time and made dismantling of the column extremely difficult. This was replaced with sleeves made of P.T.F.E. which fitted between the cone and socket comprising each joint. These sleeves

provided vacuum-tight joints, and being self-lubricating, simplified the assembly and dismantling of the column.

4.1.6. **Boilup rate experiments:** determination of boilup by heat input.

At the outset of the distillation experiments considerable thought was given to the possibility of eliminating the boilup meter and relying on power input measurements, which, together with the known heat loss from the stillpot and heater, would give the boilup rate provided the latent heat of vaporisation of the mixture were known.

The boilup meter consists of a glass device fitted into the column which causes the reflux to be diverted through a side-arm fitted with a stopcock. Under normal operating conditions the reflux flows through this side-arm. When it is required to determine the boilup rate (or more correctly, the reflux return-rate) the tap is closed and the time taken for the liquid level to reach a suitable mark is measured. The drawbacks of using such a method are:

(i) Point values of boilup rate with respect to time are obtained. If the power input or heat loss alters significantly after the measurement has been taken, distillation conditions will be altered.

(ii) The removal of a small quantity of reflux from the system, then its subsequent return upsets the thermal equilibrium of the system; this may result in a change in the material equilibrium.

(iii) The boilup meter will act as a length of open-tube distillation column, and cause some separation.

The alternative method is to measure the power input to the stillpot. Provided the heat loss from the stillpot is accurately known and remains constant and the latent heat of vaporisation of the mixture is known, the boilup rate can be determined. The heat loss must be small compared with the heat input if the method is to be accurate.

Heat loss experiments were conducted to determine the magnitude of the heat loss from the stillpot. Unsteady state and steady state methods showed the heat loss to be ~15 watts, the steady state methods giving more reproducible results. Calculation of the boilup rate from the heat input and comparison of the values obtained using the boilup meter indicated the loss to be ~20 watts. For the range of operation of the distillation column, the maximum power input was 70 watts and the minimum 30 watts. These corresponded to boilup rates of approximately 800 ml/hr. and 200 ml/hr. respectively. As the net heat inputs were therefore 50 watts and 10 watts, an alteration or uncertainty of, say, 1 watt in the heat loss would result in corresponding errors of ~2% and ~10%. It was decided in view of this error and the uncertainty in maintaining the heat loss accurately, to retain the boilup meter. The power input to the heater was also measured to provide some check: the maximum variation in the boilup rate for a given power input was observed to be 10%. Greater consistency might well have been obtained had it been possible to maintain a constant temperature enclosure surrounding the stillpot and boiler.

4.1.7. Choice of test mixture: Analysis of components.

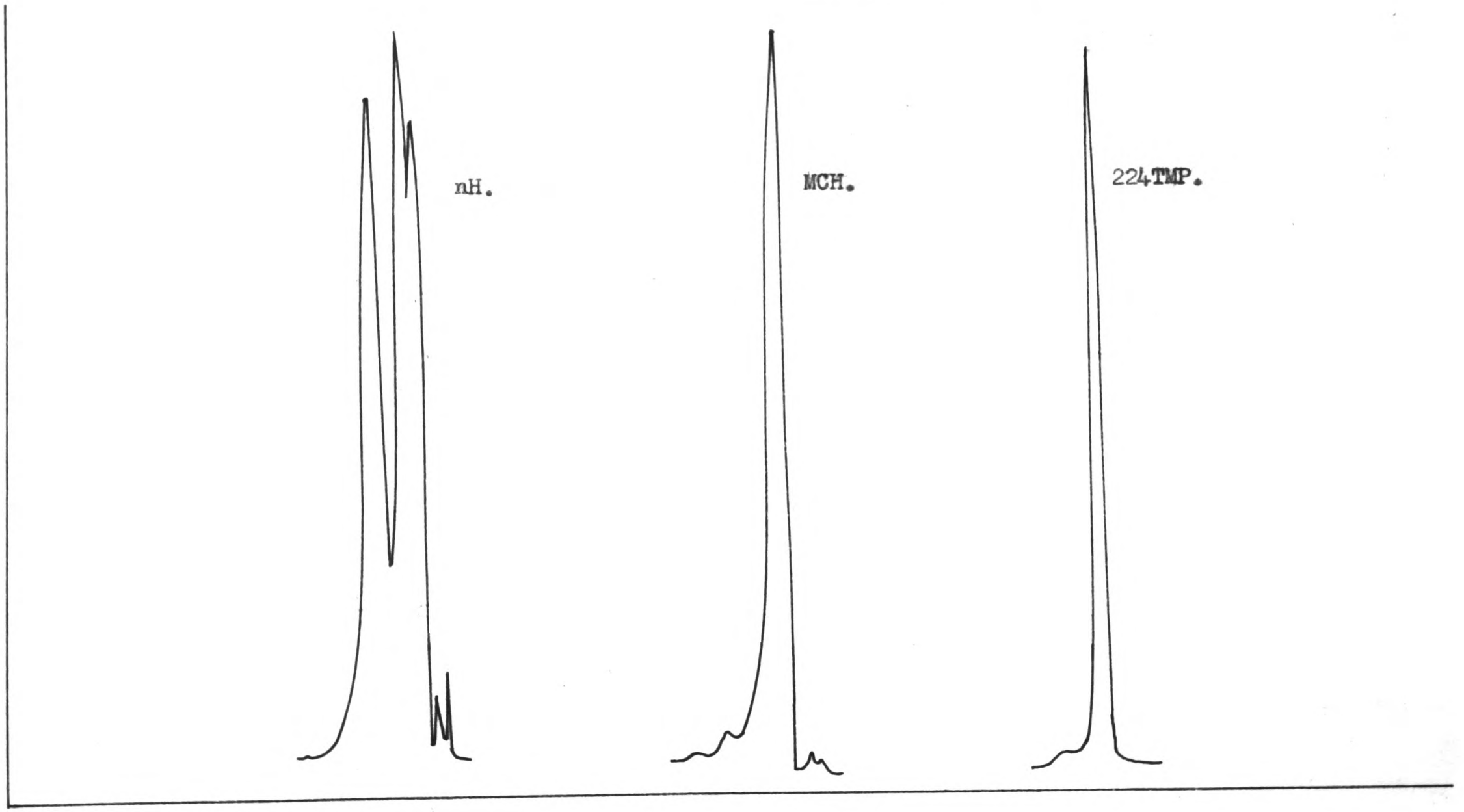
In the previous chapter, the choice of test mixtures suitable for use in a high-efficiency column was discussed. Two mixtures, n-heptane-methylcyclohexane and 2,2,4 trimethylpentane-methylcyclohexane, were considered. Although the former mixture has been used more extensively by other workers, there appears to exist some doubt as to the ideality and relative volatility. Nevertheless, this mixture was used for the earlier runs and a value of $\alpha = 1.075$ was used for calculating the number of theoretical plates. The components used were of the purest grades commercially available, the n-heptane being Hopkin and Williams Refractive Index grade, and the methylcyclohexane Kodak's Spectroscopic Grade.

As some of the results obtained showed considerable scatter, and also because doubt was expressed (55,56) as to the purity of n-heptane used in the column it was decided to analyse the components by a gas chromatography technique.

The gas chromatography column used consisted of a narrow-bore U-tube having an overall length of 6 feet, and was filled with 5% Apiczon M supported with a suitable medium. A flame ionisation detector which burnt hydrogen was used in preference to an Argon detector since the former was more sensitive and more stable, and was reliably reported (57) to have a uniform response to hydrocarbons. The carrier gas used was nitrogen and the operating temperature was 80°C. The sample size was $\sim 0{\cdot}01$ ml.

FIG.4.5

Chromatograms showing analyses of n-heptane, methylcyclohexane and 224-trimethylpentane



Chromatograms of 2,2,4 trimethylpentane, methylcyclohexane and n-heptane are shown opposite. While the first two materials (which were Kodak Spectro Grade) are seen to be comparatively pure and free from impurity, the n-heptane consists of three components A, B and C which are present in the proportions 40%, 35% and 25%. The use of the n-heptane test-mixture was therefore abandoned and 2,2,4 trimethylpentane-methylcyclohexane was used in its place.

It is not possible to state categorically whether these large amounts of impurities in the n-heptane could be responsible for a large variation in experimental results. Obviously, the two other components will be of similar type physically, since the refractive index of the impure material is identical with the literature value for pure n-heptane - unless of course this value is also based on an impure sample. As mentioned previously in the discussion of choice of test mixture, even though the appropriate physical properties of the impure n-heptane be identical with those of the pure material, it is possible that the vapour-liquid equilibria of the test mixture will be affected so as to give values of relative volatility which will vary with composition. Furthermore, different samples of n-heptane may contain different proportions of impurities which could account for existing discrepancies occurring in the literature in vapour-liquid equilibrium data and distillation studies.

Any such uncertainty is removed if a test-mixture consisting of pure components, e.g. 2,2,4, trimethylpentane-methylcyclohexane is used.

4.1.8. Column operation: Outline.

The stillpot was charged with approximately 200 ml. test mixture which contained ~ 0.2 mole fraction of the more volatile component; initially this was n-heptane but later 2,2,4 trimethylpentane was used. The heavier component was methylcyclohexane. A test run was then conducted to enable the variacs which supplied the three windings in the jacket heater to be set to the appropriate values and to determine the correct settings of the series trimmers connected to the thermistors and the position of the balance control on the Frith bridge. When a thermal balance was attained, each thermocouple pair showed no radial temperature gradient, and each wall temperature registered the boiling point of the test mixture at that point.

4.1.9. Visual observations.

Before the distillation experiments were commenced, a series of visual observations was conducted with the heating jacket heater removed, and the rotor surface was observed while in motion by means of the Dawe stroboscope.

Shahbenderian calculated that for speeds in excess of 500 r.p.m. using the 2.60 cm. diameter rotor, the rotor surface would be substantially dry. Observation of the 2.20 cm. aluminium rotor surface showed the prescence of small droplets moving slowly down the rotor at speeds greatly in excess of 500 r.p.m. The droplets moved with about the same radial speed as the rotor. It is very doubtful if they contributed significantly to the mass transfer processes in the column.

It was also observed that at speeds of ~ 2,000 r.p.m. the vapour drag on the film of liquid reflux was noticeable with the reflux describing a spiral path of about $2\frac{1}{2}$ corkscrew turns along the column length.

4.1.10 Column Operation; Detail.

For the majority of experiments conducted at lower boilup rates, and in particular when the rotor was stationary the column was preflooded by setting the variac supplying the stillpot heater so that a boilup rate of 1,200 ml/hr. was achieved. This increased the probability of even wetting on the stationary surface(s). When thermal equilibrium had been attained, the heater variac was then altered to give the required boilup rate in the region 200 ml./hr. - 800 ml./hr. In later experiments when it was realised that the heat supplied to the heating tape situated below the condenser was important in maintaining (as far as possible) adiabatic conditions, the variac which supplied this tape was adjusted until the relevant thermocouple registered an appropriate value of temperature to prevent radial heat loss. In addition, the flow of coolant through the condenser was carefully controlled, so that the reflux was not sub-cooled to any great extent. In experiments conducted with the inner cylinder rotating, the rotor was then started, and the column was permitted to run for a period of time not less than 4 hours. Periodically, the temperatures registered by the column thermocouples were recorded to check that there was no radial heat loss. During the run, boilup rate measurements were made by closing the tap on the bypass arm of the boilup meter, and measuring the time taken for the liquid level to reach the tip of the internal glass pointer. At the end of the run, samples were taken

from the condenser weir by opening one of the needle valves, and from the stillpot by withdrawing the requisite amount by means of the hypodermic syringe. The samples were collected in bottles of 1 ml. capacity and stoppered by means of a B10 stopper. This ensured that samples were airtight and so could be left for a considerable period of time before analysis, if the need arose.

The proportion of more volatile component in the sample was determined by refractive index measurement. For the n-heptane-methylcyclohexane mixture a normal Abbé refractometer was considered adequate, but a drum-reading Abbé was used for the 2,2,4 trimethylpentane-methylcyclohexane test mixture. This gave the greater accuracy necessary as the latter mixture did not have as large a difference between the refractive indices of the pure components. Also for the same separating power, the stillpot and distillate mole fractions lie closer together, on account of the lower relative volatility. All measurements were made at 25°C, and the quadratic relations given by Willingham et al. (43) were used for finding the values of mole fraction. Both mixtures were assumed to be ideal with constant relative volatilities of $\alpha = 1.075$ for the n-heptane mixture and $\alpha = 1.049$ for the 2,2,4 trimethylpentane system. Computing the values of the number of theoretical plates, N, in this fashion is preferable to using a graphical method; unless the graph is large and very carefully constructed, there will be some random error imposed on the values. To eliminate the need for hand calculation, a short Autocode programme was written for use with the Sirius computer; this programme slightly modified, was also used for recalculation of Shahbenderian's results for comparative purposes.

The number of theoretical plates was determined for various boilup rates between 200 ml/hr. and 800 ml/hr. and also at different speeds of rotation, in order to investigate the effect of Taylor number on separating power. Discussion of these and results obtained with column 2 is deferred until a later chapter.

4.2.1 Column 2.

4.2.1. Considerations of scale-up: Design of column 2.

To allow the effects of scale-up to be investigated, it was decided to construct a larger distillation column. Shahbenderian, in his research, had used a rotating cylinder mercury vapour transfer assembly which was operated with inner rotating cylinders with diameters ranging from 6·05 cm. to 13·18 cm. As the mechanical system was identical to that used in the (smaller) distillation column, i.e. a loaded cantilever system, it was considered advantageous to build the new distillation column of suitable size, around this cantilever. The cantilever was much longer and considerably more massive than that previously used, and so the critical speed was at a lower frequency. For comparable operating speeds of rotation, then, (c. 1,500 r.p.m.) the system was running at a speed far above the critical. Furthermore, it was decided as far as was practically possible, to maintain geometric similarity between the two columns and preserve the same b/r_o ratio. The $\ell/2b$ ratio is not considered important since the length of each column is long compared to the hydraulic diameter, and so entrance effects will be relatively unimportant. If the columns are geometrically similar, it is then possible to investigate the effects of scaling up a rotary concentric cylinder distillation column.

4.2.2. Cantilever and Rotor Assembly.

The rotor assembly was supported by this cantilever, which was 5 feet in length and 2 inches in external diameter. Unlike the cantilever used in column 1 it was of a hollow construction, since the weight contained in a solid rod of this size would have been impossibly heavy to support. The cantilever mounting consisted of Vee blocks and it was fixed at the top of a 12 feet length of channel. This height was necessary to allow assembly and dismantling of the column.

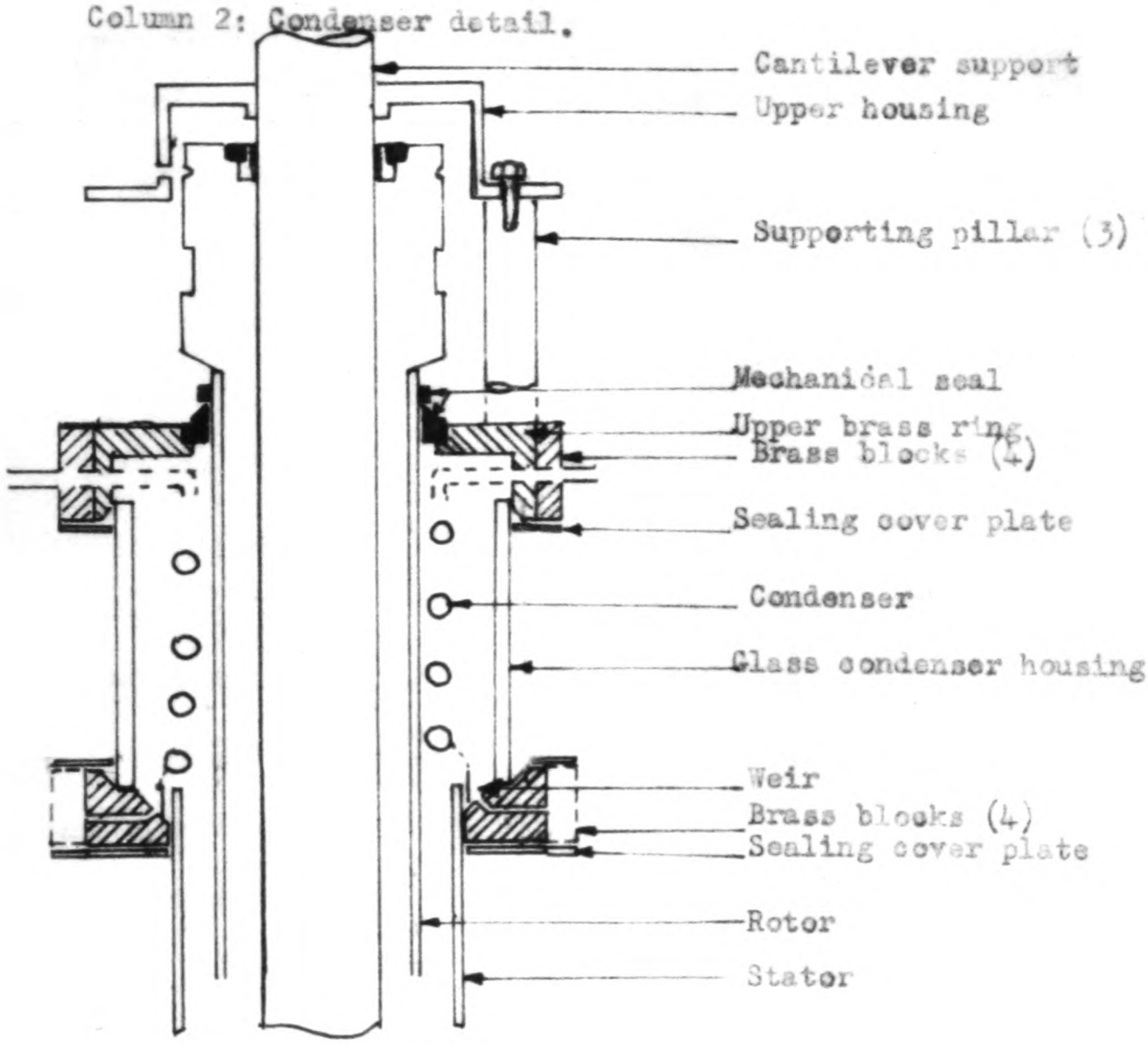
It was decided to retain the belt-drive arrangement originally used by Shahbenderian for this large apparatus. A squirrel-cage motor powerful enough to drive this much larger rotor (probably at least $\frac{1}{2}$ H.P.) would have required a very costly variable frequency alternating current generator and as suitable mechanical shaft seals had become available at reasonable cost which consumed little power, a "canned" motor arrangement was deemed unnecessary.

The rotor consisted of a 5 feet (152 cm.) length of a light aluminium alloy tube which was $3\frac{1}{4}$ inches (8.26 cm.) in external diameter. At the appropriate distance along its length a brass spider was secured by three Allen screws so that when the rotor was screwed into position, the spider engaged with the outer race of the lower bearing. The lower end of the rotor was sealed with a hemispherical plug of aluminium in which an 'O'-ring was incorporated to ensure the rotor was gastight. The heads of the Allen screws were sealed with aluminium solder.

4.2.3. Condenser section.

FIG.4.6

Column 2: Condenser detail.



The condenser section was based on that used for column 1, and is shown in Fig. 4.6. The upper brass ring supports the countercurrent condenser coil which drained into the weir. The upper side of this ring was machined with a recess so that the 'Impax' mechanical seal No. CBA 3250/2 was a push fit into it. The ring was held in position by three 1 inch diameter mild steel pillars which were attached to a flanged cover by three Allen screws. This cover was screwed on to the cantilever. A gas outlet was also provided in the ring.

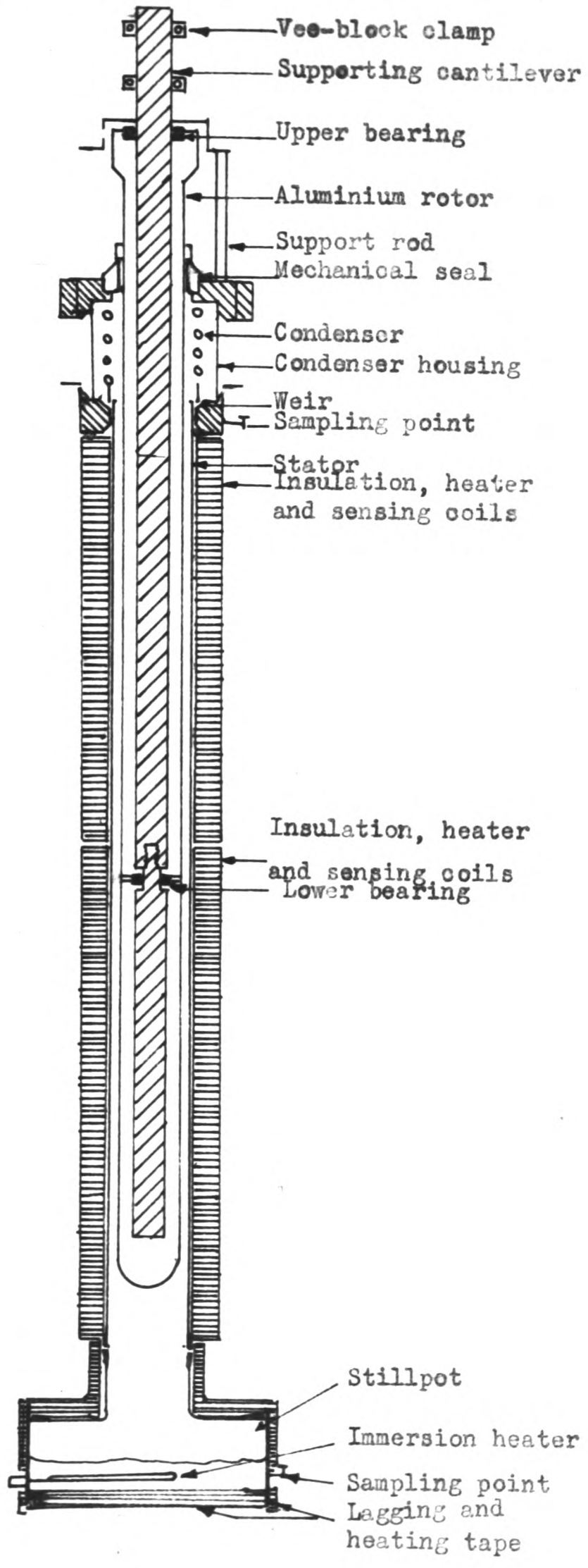
The lower brass ring which together with the upper edge of the column stator formed the weir, was held in position by two suitably shaped brass plates which rested on a frame of 2 inch by 2 inch angle iron attached to the main channel support. The reflux could be removed from the weir by the four stainless steel needle valves (identical with the two used in column 1) which were screwed into the brass ring. The glass condenser housing and the upper end of the stator were sealed by 'O'-rings and brass flanges.

4.2.4. Stator and stillpot.

The stator consisted of a $4\frac{1}{2}$ feet (137 cm.) length of Q.V.F. glass tube with the lower end made into a normal flanged end. The nominal diameter was 4 inches and the upper end was cut off horizontal and fire polished by the manufacturers. This upper edge formed the weir. The measured internal diameter of this glass was 10.75 cm.; as the external diameter of the rotor was 8.26 cms., this resulted in a radius ratio $b/r_o = 0.233$, which compared with a $b/r_o = 0.214$ for column 1. Furthermore, the gap

FIG.4.7

Diagram of Column 2.



width of 1.25 cm. was sufficient to allow the rotor to pass through the critical speed without striking the glass stator.

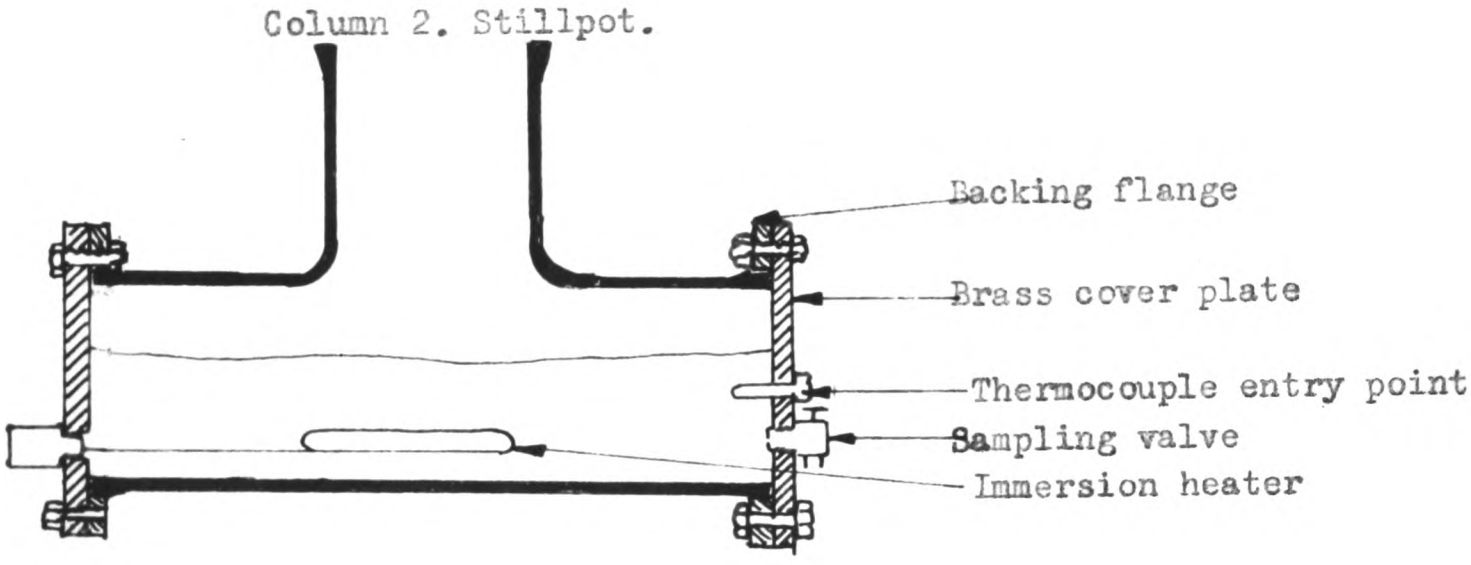
The lower end of the Q.V.F. glass tube was attached to an equal-ended Tee-piece which formed the stillpot. The two open ends were closed by means of two machined brass pieces, one of which held a 1.5 kW immersion heater, while the other was fitted with a thermocouple pocket, a stainless valve of the type used for reflux take-off, and a filling cap. The Tee-piece was held to the glass stator and the brass cover-plates by backing flanges and compressed asbestos inserts. The gaskets were of cork with P.T.F.E. sleeves. The complete column was supported at the stillpot join by a rigid frame of 2 inch by 2 inch angle iron which was bolted to the main channel support. To facilitate assembly and operation of the column a platform and handrail were erected, surrounding the column. A second, smaller platform rested on the main platform which provided a base for the motor which drove the rotor.

The column is shown diagrammatically in Fig. 4.7, while Fig. 4.8 gives details of the stillpot.

4.2.5. Adiabatic control of rectifying section.

Heat loss from the stator wall was minimised by means of an adiabatic control system similar to that used for Column 1. Two flexible jacket heaters each rated at 700 watts were tightly fitted around 4 half-sections of steam-pipe lagging which in turn was snugly fitted around the outer surface of the glass stator. The inside and outside surfaces of this lagging were wound with nickel resistance wire to give internal and external sensing coils each/

FIG.4.8


Column 2. Stillpot.
Backing flange
Brass cover plate
Thermocouple entry point
Sampling valve
Immersion heater

each with a nominal resistance of 10 ohms. There were therefore two complete sensing coils per section (four for the whole column length) one inner and one outer separated by the thermal reistance of steam pipe lagging. A thin aluminium sheet was placed between the outer surface of the lagging and each heater to minimise any local variations in heat input.

For preliminary distillation experiments, each pair of sensing coils was connected to two arms of a Wheatstone bridge network. When the resistance of the inner coil dropped as a result of the temperature falling, the resultant out-of-balance current operated a relay and caused power to be supplied to the appropriate heater. This, then, was a simple on/off system, compared with the more sophisticated half-on/full on arrangement used for column 1. After these preliminary distillation experiments, a check was made on the effectiveness of the control system by inserting thermocouple pairs in the lagging and measuring the temperature difference between the inner and outer thermocouples of each pair over a period of time. These measurements showed that the temperature difference between inner and outer thermocouples varied by as much as $\pm$ 10°C over a period of 15 minutes. An attempt to cure this trouble by adding more lagging to the outside surface of the heaters reduced the temperature difference to $\pm$ 5°C, but the cycling continued.

It was therefore decided to replace the simple Whatstone bridge system with the thermistor bridge system used in Column 1, with the sensing coils in place of the thermistors. Although the/

the resistance of each coil was much lower than that of a thermistor (10 ohms compared with 1000 ohms) and a thermistor was more sensitive to a given temperature change, it was hoped that the coils could be used, as fitting thermistors would have proved difficult. Fortunately the thermistor bridge system performed satisfactorily with the sensing coils once the variac supplying power to each jacket heater had been correctly set. The temperature difference between each thermocouple pair was estimated to be better than $\pm$ 0.3°C and the short-term cycling was eliminated.

4.2.6. Power supply : boilup rate determination.

Power was supplied to a 1.5 kW stillpot immersion heater from an 8 amp variac. Heat loss from the stillpot was minimised by insulating the brass ends with expanded polystyrene and lagging the glass with asbestos tape which was covered by a low power heating tape rated at 40 watts. The 2 amp variac supplying this tape was preset at a fixed value.

Because the net heat loss can be controlled at a small fixed value, boilup rates can be conveniently and accurately determined by measurement of the electrical power supplied to the heater provided the magnitude of the heat loss is known.

Initially, experiments were conducted to determine the net heat loss which was found to be 91.0 watts. This corresponded to a boilup rate loss of 1,550 ml/hr. As the lowest net boilup rate was 2,500 ml/hr, this heat loss was considered comparable in magnitude with the heat necessary to maintain/

maintain a boilup rate of 2,500 ml/hr. and was therefore too high. Additional fibre-glass wool lagging was added to the stillpot and the setting of the 2A variac was increased slightly. This reduced the net heat loss to 23 watts which corresponded to 400 ml/hr. boilup rate.

Power input to the heater was determined using 2 Avometers, one as voltmeter and one as ammeter. Accuracy of measurement was estimated as being better than 2%. Net heat loss was determined as follows:

Two small gaps were made in the insulation so that reflux dripping from the bottom of the metal rotor could be observed. At a given power input reflux could be seen dripping off the rotor at a certain rate. As the power input was reduced the drip rate fell until a limiting value was reached. Decreasing the power input further caused no further fall in drip rate. The power input corresponding to the drip rate slightly above the minimum rate was taken as being equal to the net heat loss. So that this loss remained unaltered during distilling, the small gaps in insulation were left.

4.2.7. Mechanical performance of rotor.

Initially, the rotor was driven by a 0.25 H.P. D.C. motor supplied by an electronic speed control unit, which enabled the rotor to be run at speeds between 200 r.p.m. and 2,000 r.p.m. Unfortunately, this motor was not powerful enough, and burnt out after some hours use. A 3 phase 0.5 H.P. A.C. motor running at 960 r.p.m. was then used. By changing belts and pulleys/

pulleys four rotor speeds of 1,000, 1,200, 1,670 and 2,200 r.p.m. could be obtained. As this driving system was inconvenient, it was replaced by a 0.5 H.P. Allspeeds Kopp variator, driven by a 3 phase 0.5 H.P. 960 r.p.m. AC motor, which had continuously variable output speeds from 300 r.p.m. - 3000 r.p.m. This was coupled to the column rotor by means of a Vee belt to give rotor speeds of 300 r.p.m. - 2000 r.p.m. Above this top speed, belt slip became excessive presumably due to overload. Within these limits the Kopp variator performed very well.

The critical rotor speed was found to be C. 600 r.p.m. Below this speed, smooth running down to 300 r.p.m. was obtained, and the rotor ran well between the critical speed and 2000 r.p.m. No difference in stability of rotor operation was observed when the rotor was run hot. Only once did oscillation appear at speeds other than the critical. This fault was due to a section of the cantilever working loose and was easily rectified.

4.2.8. Additions to the rotor : provision of wipers and wires.

Because it was not possible to have the glass stator mounted exactly vertically and its upper edge ground square, thereby ensuring even reflux distribution, 2 P.T.F.E. wipers were fitted to the upper end of the rotor. These wipers were made from 2 P.T.F.E. strips each 0.25 in. cross-section and 4 in. length. They were hinged at their upper ends on to a collar which was constructed from two semicircular pieces of aluminium. These pieces were tightly clamped to the rotor. When the rotor was turned the wipers tended to fly outwards against the glass, carrying around any reflux present. Visual observations described in section/

section 4.2.9. showed that reflux distribution was satisfactory at boilup rates investigated.

When the principal distillation experiments were finished, the effect of stirring the liquid film of reflux was investigated. Two wires of drawn brass were strung the length of the rotor by two clamping split rings made of brass. The tension in each wire was low so that when the rotor was turned, most of the wire length was thrown against the glass stator thereby agitating the liquid film.

4.2.9. Visual observation of reflux.

Visual studies of the reflux were made as follows:

i) on the stator wall using normal illumination

ii) on the rotor surface using stroboscopic light

iii) on the stator wall with sweeping wires attached to the rotor using stroboscopic light.

These observations were conducted:

(a) with the jacket heaters completely removed

(b) through a 1" circumferential gap between the two heaters at the midpoint of the column length.

Condition (a) corresponded to non-adiabatic operation of the column while conditions (b) approximated closely to adiabatic operation.

For each set of conditions the rotor speed was varied between 850 r.p.m. and 1900 r.p.m. which corresponded to a Ta range of $7240 < Ta < 16150$.

At speeds of rotation up to 1400 r.p.m. the reflux behaved as a rippling wetted film. At 1600 r.p.m. the ripples had almost completely disappeared and were replaced by a pattern of rivulets which were inclined at an angle of c. 20° to the vertical. At the/

the highest speed of 1900 r.p.m. these rivulets were more pronounced but were still of the same form. Under these non-adiabatic conditions it was not possible to tell whether the reflux was evenly distributed around the stator wall. However when observations were made with the jacket in place (with the 1" circumferential gap) under conditions which were close to those of adiabatic operation, a uniform rippling film was observed at the rotational speeds of 850 r.p.m. and 1275 r.p.m. at the lowest boilup rate of 2500 ml/hr., which corresponded to vapour phase $Re_V = 278$ or a liquid phase $Re_L = 20$. At the highest rotational speed of 1900 r.p.m. at this low boilup rate, rivulets could be observed; between the rivulets, which were spaced a distance of 2-3 cm, no liquid could be seen, which was in contrast to all other observations at boilup rates higher than 2,500 ml/hr. at this high speed of rotation. This is good evidence for assuming complete and even wetting of the stator by reflux at all conditions except that of low boilup rate of 2500 ml/hr. and high rotor speed of 1,900 r.p.m.

Under non-adiabatic conditions it was possible to observe small droplets on the rotor surface with the aid of stroboscopic light, at the lowest rotational speed in the range 850 r.p.m. - 1900 r.p.m. Their diameters were of the order of 2.0 mm. and their density was 10-20 per sq.cm. on the rotor surface. Behind the trailing edge of many of these droplets were striations. As the rotational speed was increased the number of striations decreased, and the size and number of droplets decreased. The rate of descent of these droplets also fell as rotor speed was increased/

increased; at 1000 r.p.m. rate of descent was c. 3 cm/sec. which at 1400 r.p.m. had decreased to c. 1.5 cm/sec. Also at 1400 r.p.m. the striations had completely disappeared. While the droplet size was of the order of 1.0 mm. at the top speed of 1900 r.p.m. the droplets had almost completely disappeared apart from a few of c. 0.1 mm. diameter which were moving horizontally. The few observations conducted with the lagging in place did not conflict with these findings. A single observation (without lagging) at the rotor speed of 240 r.p.m. showed the rotor surface was substantially wet. Conclusions from these findings were:

i) There is no evidence of a substantial mass transfer film on the rotor in the speed range 850-1900 r.p.m.

ii) There is no evidence of condensation along the rotor length.

The third set of visual observations, of the stator wall with wires attached to the rotor, was made with the jacket heaters in place. Observations were conducted at speeds of 850, 1275 and 1900 r.p.m. and 2,500, 6,000, and 10,000 ml/hr. At the lowest rotor speed there was slight turbulence surrounding the wires at all the above boilup rates. This was shown by an abnormally disturbed region of reflux film in the wire's immediate vicinity. Increasing the speed to 1275 r.p.m. caused fine bubbles of vapour to appear entrained by the action of the wires. The width of this band of entrainment was 1.0 - 2.0 cm. Increasing the speed further to 1900 r.p.m. caused this entrainment to be more vigorous. As the boilup rate was increased at this speed of rotation waves of liquid were periodically seen to sweep round the surface of the reflux at a speed slower than that of the rotor.

Where/

Where appropriate, further reference will be made to these phenomena in the discussion of results in chapter V.

4.2.10. Column operation under conditions of distillation.

At the beginning of a series of experiments the stillpot was charged with 2 litres of test mixture which contained c. 0.2 mole fraction of the more volatile component. The test-mixture used was 224 trimethylpentane-methylcyclohexane: both these components were supplied by Kodak Ltd. and were Spectro Grade quality. The immersion heater was then supplied with full power until reflux appeared at the top of the column, then it was set to give the appropriate boilup rate. At the same time, the jacket heaters were switched on and the variacs supplying these were preset to give the appropriate power inputs which had been determined previously. The rotor was then set in motion and the supply of coolant adjusted so that as little sensible heat as possible was removed from the condensate. When thermal equilibrium had been established, the column was allowed to run for a period of 4-5 hours to ensure that material equilibrium was established. Stillpot and distillate samples were then withdrawn and analysed for mole fraction of more volatile component using a drum-reading Abbé refractometer. During each trial thermocouple measurements were made of differential temperatures in the upper and lower jacket heaters, to ensure the absence of heat loss from the rectifying section.

When samples had been taken for analysis, either the rotor speed or the boilup rate was altered, and the column again allowed to reach material equilibrium. In this way, it was possible to obtain/

obtain 3 readings per day. A low supply of heat to the column was left on overnight, so that a long warm-up period in the morning was not necessary. From time to time, additional material was supplied to the stillpot to replenish the contents removed by sampling.

After the principal experiments had been conducted with this column, two sweeping wires were attached to the rotor in such a manner (described in section 4.2.8.) that they swept the reflux film continually. A series of experiments was then carried out. Because of the construction of the column it was not possible to have the whole length of the wire disturbing the reflux - a portion of the wire cut through the vapour. It was therefore necessary to conduct further check experiments with the wires tightened so that they stirred the vapour only.

The results and implications of these experiments are discussed in the following chapter.

Chapter V

5.1 Introduction.

In this chapter, the results of the present experimental study are compared with values predicted from theory. Results of certain previous investigators which were referred to in Chapter II are also included. To simplify presentation the chapter is divided into two principal sections, the first dealing in detail with the theory, the inferences drawn from it, and the assumptions necessary for comparison of results estimated from the theory with experimental results. In the second section the experimental results are compared with these estimated values.

5.2 The Westhaver/Shahbenderian/Flower theory

In Chapter II, a theory is presented which was developed by Westhaver for the operation of open and concentric tube fractionating columns. Subsequently Shahbenderian extended this treatment to include the case with the inner cylinder rotating such that the vapour flow was laminar + vortex. This theory was based on classical steady-state mass-transfer theory and was chosen to predict the performance (in terms of separating power) of rotary concentric-tube fractionating columns because there is evidence that in certain cases it can predict column performance under specified conditions of operation.

In Chapter II various sets of mass transfer data were presented which could be correlated in the form:

$$Sh \propto (Ta)^{0.5}\left(\frac{r_o}{r_1}\right)^{0.25} f(Sc) \qquad 5.1$$

where Sh may be defined

$$Sh = \frac{kb}{D}$$

Shahbenderian/

Shahbenderian has shown that

$$H_v = \frac{Vb}{k}$$

or $$H_v = \frac{Re}{k}$$

Eliminating k and substituting in 5.1 gives:

$$\frac{H_v}{b} \quad (Ta)^{-0.5} \; (Re) \; \left(\frac{r_1}{r_o}\right)^{0.25} \quad f(Sc) \qquad 5.2$$

Where there is liquid-phase resistance present Westhaver predicted that, in the case of a laminar film of reflux

$$H_L = \frac{33}{140} \frac{\bar{u}_L w^2_L}{D_L} \qquad 5.3$$

In the presence of rippling, the value of H_L will be less than that predicted. The total H.E.T.P. is equal to:

$$H_T = H_L + H_V$$

5.2.1 Inferences and assumptions in the present work

Inference 1. In the absence of any liquid-phase resistance to mass transfer, the Westhaver/Shahbenderian theory predicts that the H.E.T.P. should vary inversely as the square root of the rotor speed and directly as the boilup rate. This inference rests on the two assumptions, A and B:

A That the interfacial area remains constant over all operating conditions.

In the larger Column II, rotor speeds were varied between 850 - 1900 rpm. Before the distillation experiments were started an extensive series of visual observations of rotor and stator appearance was conducted with normal and stroboscopic light over the range of boilup rates 2500 - 10000 ml/hr. From these visual observations/

observations described in detail in Section 4.2.9 (Chapter IV) and from the reproducibility of distillation experiments later conducted it may be concluded that:

a) The outer wall was completely wetted with reflux

b) The rotor surface was substantially dry, the influence of the observed droplets being negligible.

The interfacial area was not therefore altered by variable wetting of either surface. Under many operating conditions the liquid film was not laminar, but rippling. At the lowest and intermediate rotor speeds of 850 and 1275 rpm. (corresponding to Ta = 7240 and Ta = 10,750 respectively) rippling was observed at boilup rates between 4,000 ml/hr. and 10,000 ml/hr. This rippling increased in amplitude with boilup rate, and was absent at the lowest of 2,500 ml/hr. Assuming a value of $\nu_L = 0.0041$ cm^2/sec for the liquid kinematic viscosity of the test-mixture used, the range of boilup rates 2,500 ml/hr. - 10,000 ml/hr. corresponded to Re_L in the range $20 < Re_L < 80$. At a $Re_L = 20$ the liquid flow was observed to be laminar. By extension of a theory propounded by Kapitza (59), Portalski (58) has predicted the onset of a pseudo-laminar (rippling) regime when:

$$3.8\ Re_L = 5.33 \left(\frac{\nu_L \delta^3}{g}\right)^{1/6} \qquad 5.3.4$$

The critical Re_L for the test-mixture used in the distilling conditions in Column II was predicted by equation 5.4 as $Re_L = 20$, which is in agreement with the experimental observations. Tailby and Portalski (60) have obtained independent verification of equation 5.4 by observation of wetting rates of 82% glycerin solution on a stainless steel plate. Their observed and estimated values were $Re_L = 7$ and $Re_L = 4.9$ respectively.

At/

At the highest rotor speed of 1,900 rpm. (Ta = 16,150) the rippling was replaced by a series of troughs and striations of reflux which were nearly vertical. No dry patches were observed on the stator surface. The effect of rippling and the pattern of striations is to increase the surface area slightly. In the former case this can be predicted using an expression derived by Portalski:

$$\Delta s = \frac{w_L \pi a}{2} \left[1 + \left(\frac{g a \lambda^3}{16 w_L \delta \pi^3}\right)^2\right]$$

where Δs is the fractional surface area increase.
At a boilup rate of 8,000 ml/hr. ($Re_L = 64$) the estimated surface area increase is $< 0.3\%$. Portalski (60) working with 82% glycerin has independently confirmed this relation to be approximately correct. While it is not possible to estimate the surface area increase due to the striations caused by the highest rotor speed, there is no reason to suppose they will be greatly different from the increase arising from rippling. Those two surface disturbances are unlikely, therefore, to alter the surface area significantly and assumption A, that the interfacial area does not alter with operating conditions is probably essentially correct.

Inference I also rests on the assumption:

B That the vapour flow regime is laminar + vortex.

From the data of Becker (16) Flower (22) and Todd (23) given in Fig. 2.5 the vapour flow cannot have been laminar but must at least have been in the laminar + vortex regime. The vapour viscosity value was assumed $\nu_v = 0.0306$ cm^2/sec. From the work of Flower it is unlikely that the flow was turbulent + vortex at the lowest rotor speed corresponding to Ta = 7240 even making allowance for the uncertainty in the assumed value of ν_v; but the vapour flow may have/

have been turbulent + vortex at the highest Ta = 16150. It is probable that at the lowest boilup rate of 2500 ml/hr. (corresponding to Re_V = 280) the vapour is laminar + vortex throughout the Ta range.

5.2.2 Inference II

If maximum weight is given to the liquid side resistance a second, more complex, dependence is obtained by combining equations 5.2 and 5.3:

$$H_T = H_L + H_V = X.(Q)^{4/3} (Sc_L) + Y(Q) (Ta)^{-0.5} f(Sc)$$

This form of dependence is based on two further assumptions:

C That the reflux film is in laminar flow

For many conditions of operation in column II we have shown both experimentally and theoretically from Portalski's relation in section 5.2.1 that this is not true, and that above boilup rates of 2,500 ml/hr. (e.g. 4,000 ml/hr corresponding to Re_L = 32 and Ta = 10,750) the reflux film is rippling. There is much experimental evidence for mass transfer increase in liquid phase controlled systems in rippling film flow as compared with laminar film flow. Emmert and Pigford (61) studied absorption and desorption of CO_2 and O_2 in water, conducting their experiments with and without surface active agents. Typical results were: oxygen-water at $Re_L \sim$ 250, no rippling H_L = 5.7; rippling H_L = 2.0: carbondioxide-water, $Re_L \sim$ 200, no rippling H_L = 4.5; rippling H_L = 1.0. Other similar mass transfer increases were reported by Kamei and Oishi (62) and Brauer (63) who obtained 125% increase in mass transfer at Re_L = 40 and 220% increase at Re_L = 60. These increases due to rippling are only in partial agreement with those estimated/

estimated from an expression derived by Ruckenstein (64) who predicted an increase of 130% in mass transfer at both $Re_L = 40$ and $Re_L = 60$. On the other hand, Portalski (65) concludes from a theoretical study of rippling films that at wavelengths $3\lambda/4$, $7\lambda/4$, ... etc., separation of the liquid occurs on account of the thin film which results in the formation of eddies. In a liquid phase controlled system, the estimated increase in mass transfer (i.e. reduction in H_L) is probably greater than the above experimental data suggests. For most of the conditions of operation, assumption C is therefore invalid. But at the lowest boilup investigated ($Re_L = 20$) and lowest and intermediate rotor speeds, the reflux flow is probably laminar; assumption C will therefore be correct for those conditions.

Assumption D of a numerical value for the ratio of vapour and liquid phase resistances. This numerical value will change with the operating conditions as the effective liquid diffusivity D'_L will alter as the mass transfer in the liquid is improved by increased rippling at the higher boilup rates. At the lowest boilup rate, however, it should be possible to predict H_L from Westhaver equation 5.3 provided the value of liquid diffusivity is known. Unfortunately, both for the two test-mixtures used in the present series of experiments and also for many other test-mixtures no values of the liquid diffusivity have been determined experimentally at their boiling-points. For the test-mixture 2.2.4 trimethylpentane methylcyclohexane Willingham et al (4) quote a value of $D_L = 5.0 \times 10^{-5}$ cm^2/sec. No reference is given. Wilke and Pin Chang (66) present an empirical relation based on Eyring theory and the Stokes-Einstein relation:

D_L/

$$D_L = 7.4 \times 10^{-8} \frac{T(M)^{0.5}}{V_M^{0.6}}$$

Where comparison is possible, an average deviation between calculated and experimentally determined values may be made as follows. The molal volume, V_M, may be estimated by the method of atomic contributions of Le Bas (68). Kamal and Canjar (67) have developed a more fundamental relation, which involves the ratio of the occupied volume per molecule to the total volume per molecule (υ_o/υ). They recommend this ratio be accurately determined as described by Collins and Navidi (78) from measurements of velocity of sound in the medium. They found a mean deviation not greater than 10% between predicted and experimental values for various systems. Hutchison (69) examined the systems acetone-benzene, chloroform-benzene and chlorobenzene-benzene at different temperatures. His comparison of the estimated and measured values of D_L using Kamal and Canjar's method for these systems gave predictions such that the experimental values were between 10%-70% high.

In the absence of values of the ratio (υ_o/υ) from velocity of sound measurements only the method of Wilke and Pin Chang is used to estimate D_L for the test-mixture. Values of D_L predicted by this relation for the test-mixture 2.2.4 trimethylpentane-methylcyclohexane is $D_L = 4.4 \times 10^{-5}$ cm^2/sec at infinite dilution, or $D_L = 4.6 \times 10^{-5}$ cm^2/sec at 0.2 mole fraction. This method of estimation for a particular 2 component system is extremely inaccurate, and at best, may only give an order of magnitude value for D_L.

5.2.3 Inference 3

It should then in principle be possible to obtain an absolute estimate/

estimate of the column performance for a given set of operating conditions by means of

Assumption E, I i) an absolute value of the vapour diffusivity

ii) the function f(Sc) in equation 5.1 or 5.2

iii) a value of the constant of proportionality in equation 5.2.

Assumptions C and D may be excluded, and H determined as follows:

H_V can be deduced from equation 5.2 as i) and ii) and iii) are known from experiments with vapour-side controlled systems. The effective diffusivity of the rippling film can then be deduced from observations of the variation of column performance with rotor speed or boilup rate in the neighbourhood of the relevant operating conditions. This value of effective diffusivity could then be used to predict H_L for the required conditions of operation, hence the height equivalent to a theoretical plate $H_T = H_L + H_V$.

5.2.3.1 Vapour diffusivities

Although there are more experimental determinations and correlations available for vapour diffusivities, no data are available for many binary pairs used as test mixtures. This being the case, it is necessary to resort to the use of various methods of prediction from physical and thermodynamic properties. Gilliland (70) presented a correlation based on classical kinetic theory assuming molecules behave as hard spheres:

$$D_V = 0.0043 \frac{T^{3/2}}{P(V_1^{1/3} + V_2^{1/3})^2} \left(\frac{M_1 + M_2}{M_1 M_2} \right)^{1/2}$$

Arnold (71) presented a similar correlation which included the Sutherland constant in an attempt to correct for molecular interactions:

$$D_V = \frac{0.00837\ T^{3/2}}{P(V_1^{1/3} + V_2^{1/3})(1+\frac{G_{12}}{T})} \left(\frac{M_1+M_2}{M_1 M_2}\right)^{\frac{1}{2}}$$

where G_{12} is the Sutherland constant

$$G_{12} = \left[\frac{2\sqrt{V_1^{1/3}\ V_2^{1/3}}}{V_1^{1/3} + V_2^{1/3}}\right]^3 \sqrt{G\ C_2}$$

and C_1 and C_2 may be estimated from the boiling temperature

$$C = 1.47\ T_b$$

for a wide range of binary pairs, the correlation of Gilliland gives an average deviation of 16%, although (as with the correlations used for determining liquid diffusivities) the difference for an individual binary system between experimental and predicted values may be considerably greater. Arnold's correction factor reduced this average deviation between experimental and theoretical values to 10%.

Modern kinetic theory attempts to account for attractive and repulsive forces between molecules. A common potential energy function is the Lennard Jones (6-12) function used for non-polar molecules:

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

and r the distance between molecular centres. The force-constants σ and ϵ are properties of the molecular species. Hirschfelder, Curtis and Bird (72) have developed an approximate relation for vapour diffusivity:

$$D_V = \frac{0.001858\ T^{3/2}\ (M_1 + M_2)^{\frac{1}{2}}}{P\ \sigma_{12}^2\ \Omega_D\ (M_1 M_2)^{\frac{1}{2}}} \qquad 5.5$$

where/

where σ_{12} is the arithmetic mean of the force-constants σ_1 and σ_2 and Ω_D is the collision integral, values of which have been tabulated by Hirschfelder (73) as a function of $(\frac{Tk}{\epsilon_{12}})$, where ϵ_{12} is the geometric mean ($\epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2}$) of ϵ_1 and ϵ_2.

For many simple molecules, values of ϵ and σ have been determined from experimental viscosity data. These values of and σ can thenbe used for estimating D_V. Good agreement is obtained between the experimental and theoretical values in many cases. However, for the test mixture components under consideration, no experimental viscosity data are available, and it is necessary then to estimate values of the force constants from approximate relations with the critical constants (74):

$$\frac{\epsilon}{k} = 0.77\ Tc$$

$$\text{and } \sigma = 0.833\ Vc$$

Hirschfelder emphasises that these two relations given above and other similar relations are no more than rough estimates. Thodos and Stiel (75) developed relations which they claimed were more accurate, while Wilke and Lee (76) replaced the constant term (0.001858) in equation 5.5 by an empirical function of molecular weights, and in the absence of viscosity data estimated the force constants from molal volumes and boiling temperatures. Recently, Chen and Othmer (77) have presented a generalised correlation for vapour diffusivity from the critical data. In addition to presenting more complex relations for the force constants in terms of critical data they developed an expression for the collision integral Ω_D in terms of the force constants. A mean deviation of 3% between experimental and predicted values was claimed, although in a particular case, this may be considerably greater.

Although/

Although critical data have been measured for n heptane and 2.2.4 trimethylpentane, they have not for methylcyclohexane, and must be estimated. This introduces further uncertainty into the estimation of D_V. Values of critical data used are those given in Chapter III on p 40. Diffusivity values for n-heptane-methylcyclohexane are given in the table below:

Table 5.1

Values of D_V (cm^2/sec)	Correlation
3.9×10^{-2}	Gilliland (70)
1.4×10^{-2}	Arnold (71)
3.4×10^{-2}	Hirschfelder (72)
2.4×10^{-2}	Wilke and Lee (76)
3.1×10^{-2}	Chen and Othmer (77)

This variation demonstrates the wide range which results from using different correlations. In the absence of the necessary experimental data for values of D_V or experimental values of viscosity variation with temperature to enable the force constants to be determined (or at the very least, critical data of methylcyclohexane) the method of Chen (77) is recommended. For the test-mixture of 2.2.4 trimethylpentane-methylcyclohexane a value of $D_V = 0.029$ cm^2/sec was calculated.

In addition to the uncertainty of the vapour diffusivity values, the relation between H_V and Sc_V (and hence between H_V and D_V) is unknown when the vapour flow is laminar + vortex. The function f(Sc) would require to be determined either from mass or heat transfer data varying either Sc or Pr. It would also be possible from such experiments to determine a value for the constant in equation 5.2 which also is unknown.

In/

In the present experimental work, it has been possible to obtain an absolute estimate of column performance by a graphical solution of this problem (Inference III), details of which are given later. A corollary of Inference III is that if Assumptions A-E are correct, it will be possible to predict the absolute values of H_L and H_V and obtain an absolute estimate of column performance in the absence of experimental data.

5.2.4 Inference IV

The Westhaver-Shahbenderian-Flower treatment also predicts how a column performance (in terms of no. of theoretical plates) will depend on the column dimensions. In the absence of liquid-side resistance and using the same test-mixture (and hence same f(Sc)) the following relation is deducible from equation 5.2:

$$\frac{(H_V)_2}{(H_V)_1} = \frac{b_1}{b_2}\,\frac{Re_2}{Re_1}\left(\frac{Ta_1}{Ta_{u2}}\right)^{0.5}\left(\frac{r_1}{r_o}\right)_2^{0.25}\left(\frac{r_o}{r_1}\right)_1^{0.25}$$

where the subscripts 1 and 2 refer to the columns 1 and 2 respectively. In addition, if experiments are conducted for identical values of Re and Tu this reduces to:

$$\frac{(H_V)_2}{(H_V)_1} = \left(\frac{(r_o)_2 - b_2}{(r_o)_2 b_2^4}\right)^{0.25}\left(\frac{(r_o)_1\, b_1^4}{(r_o)_1 - b_1}\right)^{0.25}$$

A second, more complex form of relation is obtained if maximum weight is given to liquid side resistance as in Inference II provided assumptions C and D are correct.

5.3 Experimental results Column II

Two sets of experiments were conducted with column II:

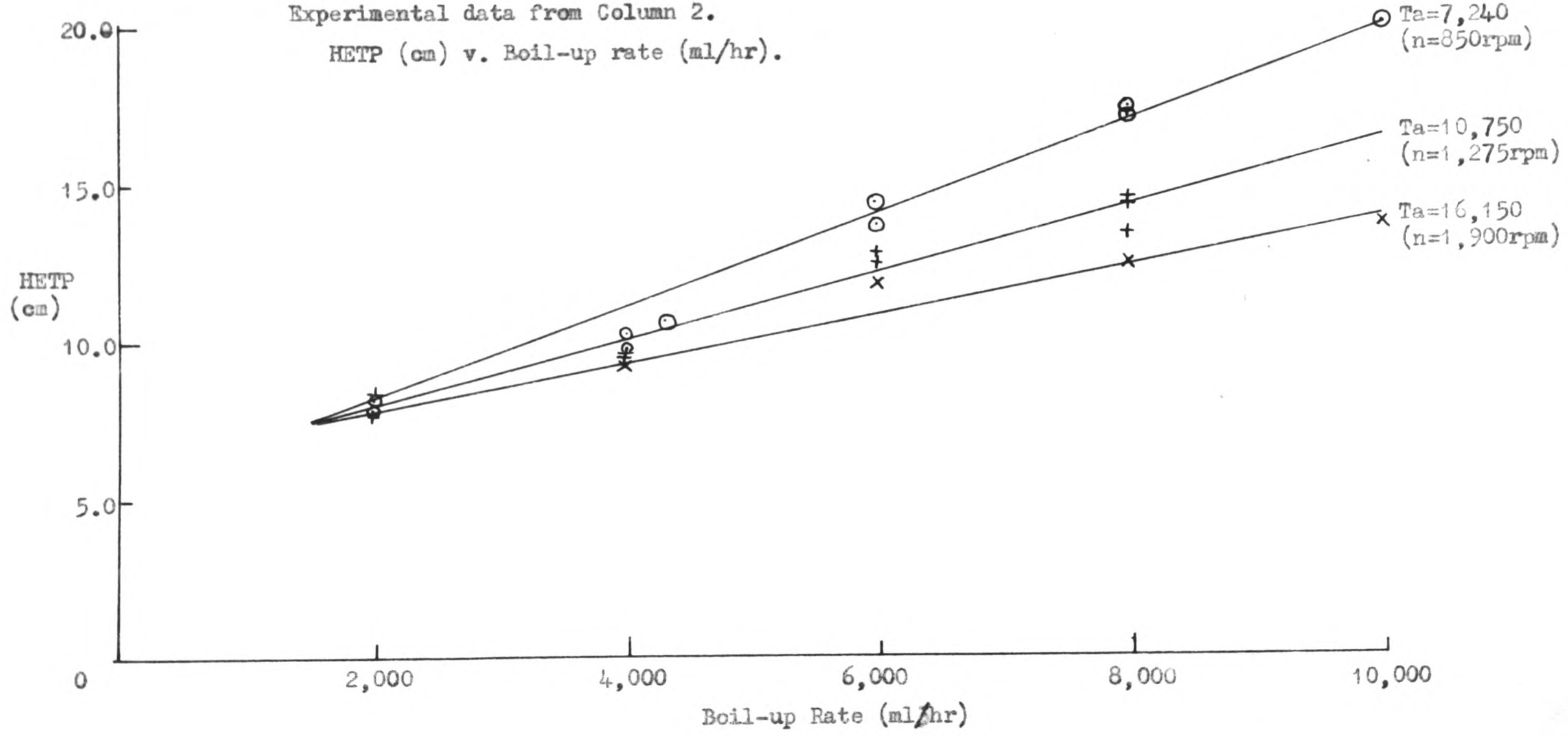
a) operating as a rotary concentric tube column with no additional stirring of the liquid phase.

b)/

FIG.5.1

Experimental data from Column 2.

HETP (cm) v. Boil-up rate (ml/hr).



b) with sweeping wires attached to the rotor so that a major portion of the reflux was stirred when the rotor was turned. With condition b) it is possible that Assumption A - constant interfacial area - may be invalidated.

5.3.1 Experiments without sweeping wires

Preliminary experiments were conducted at rotor speeds of 1,000 and 1,470 rpm. over a boilup rate range 2,500 - 8,000 ml/hr. The large scatter from these data confirmed subsequent findings that the stillpot had been inadequately lagged which resulted in varying heat losses from day to day and the simple on-off control system (described in Chapter IV) was not functioning correctly. After these faults were corrected, a further set of experiments was conducted.

These principal experiments were performed over the ranges $2{,}500 < Q < 10{,}000$ ml/hr. and $850 < n < 1{,}900$ rpm. Assuming a value of $\nu_v = 0.0306$ cm^2/sec., these corresponded to $278 < Re_V < 1{,}110$ and $7{,}240 < Ta < 16{,}150$. The experimental accuracy of these results was estimated to be not worse than $\pm$ 0.3 theoretical plates as determined by drum-reading Abbe refractometer. The results are shown in Fig. 5.1 opposite. Fig. 5.2 shows the expected variation of H with Q at the three Ta values if the vapour phase was controlling.

Comparison of these two figures immediately makes obvious:

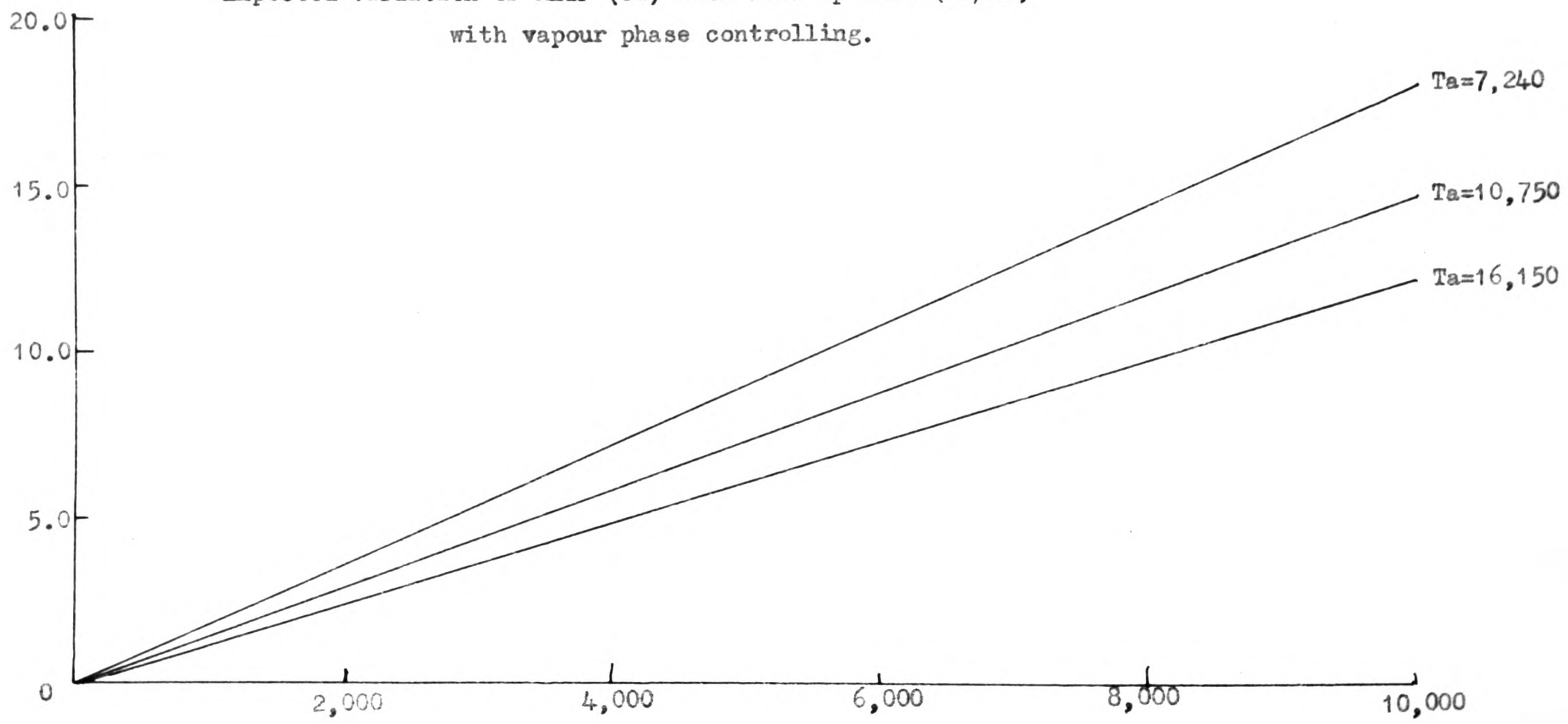
i) there is no indication that the lines meet on the axis H = 0. There is therefore no justification for assuming that $H.\alpha(Ta)^{-0.5}$.

ii) H $\not\propto$ Q, because the lines do not all meet at the origin. On assumptions A and B (constant interfacial area and L + V motion in the vapour phase) the mass transfer is not therefore controlled solely by the vapour phase.

These/

FIG.5.2

Expected variation of HETP (cm) with Boil-up rate (ml/hr)
with vapour phase controlling.



These two conclusions are drawn from Inference I. Further consideration of Fig. 5.1 shows (inference II):

iii) the shape of these curves cannot be explained with the aid of assumptions C and D (laminar flow of reflux film and a numerical ratio between vapour and liquid resistances respectively). The curves show H is less dependent on boilup rate than would be predicted by vapour-phase resistance alone. The addition of a laminar film liquid phase resistance to vapour-phase resistance would cause the overall H [$H = (H_V) + (H_L)_{lam.}$] to increase more rapidly with boilup rate. This is because $(H_L)_{lam} \propto Q\, W_L$, and $W_L \propto Q^{1/3}$; hence $(H_L)_{lam} \propto Q^{4/3}$.

iv) By a graphical solution of the problem outlined in 5.2.3, an absolute estimate of column performance may be obtained, by assuming a value of f(Sc) and apparent liquid diffusivity obtained from measurements of variation of H with Ta. This graphical solution is shown in Fig. 5.3 which results from superimposing Figs. 5.1 and 5.2. The slopes of the constructed lines which pass through the origin are such that $S_1 : S_2 : S_3$ as $Ta_3^{0.5} : Ta_2^{0.5} : Ta_1^{0.5}$. This determines the relative slopes of these lines, but not their actual slopes, which were fixed by trial and error such that, at a given boilup rate, the distances between each experimental line and corresponding constructed line were equal. These three vertical distances, are the values of H_L at the three Ta and a fixed boilup rate. This graphical solution gave the following positions of the constructed lines:

at Ta = 7,240 (0,0) and ($H = 18.0$ $Re_V = 1,110$)

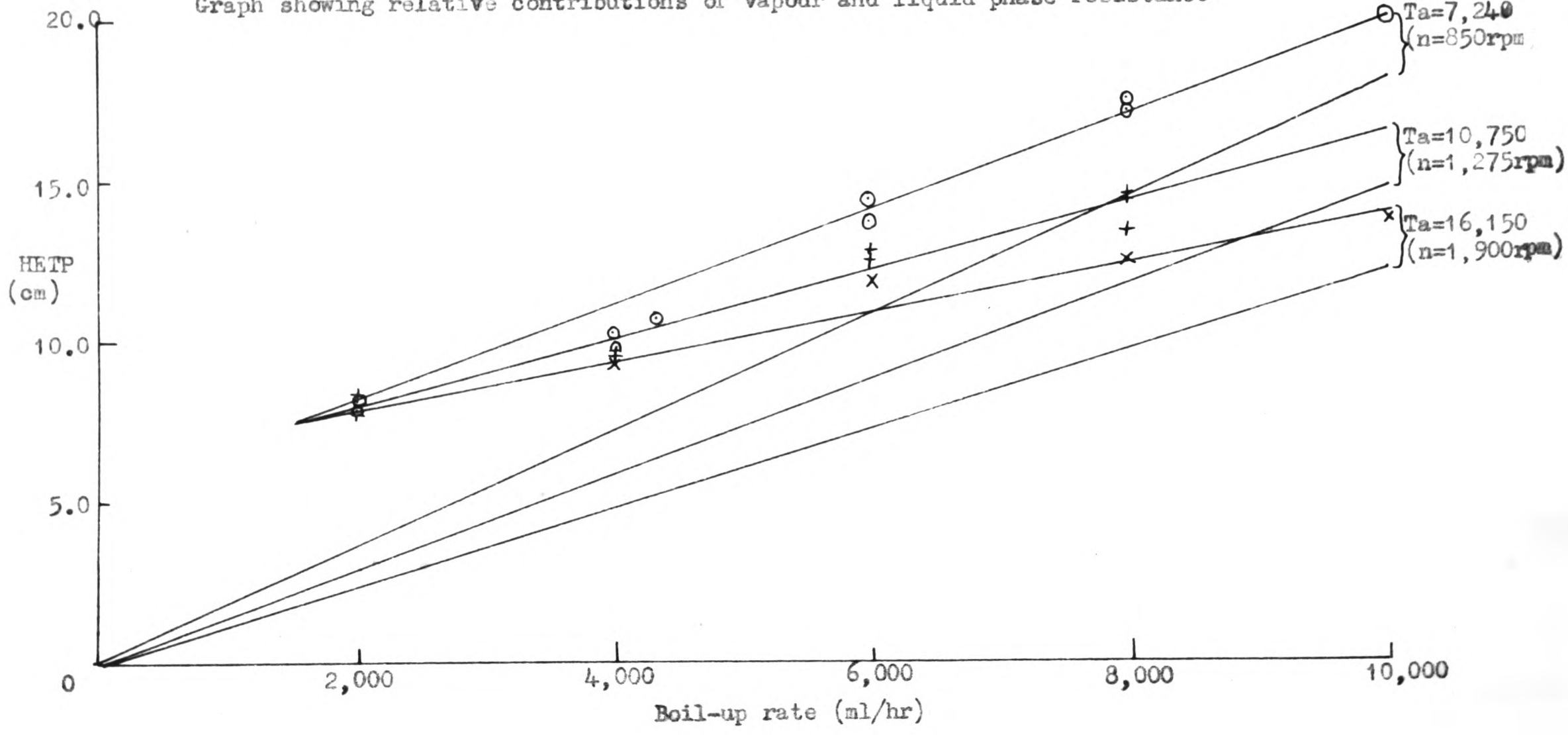
10,750 (0,0) and ($H = 14.7$ $Re_V = 1,110$)

16,150 (0,0) and ($H = 12.2$ $Re_V = 1,110$)

This/

FIG.5.3

Graph showing relative contributions of vapour and liquid phase resistance



This construction gives reasonable agreement of $(H_L)_1$, $(H_L)_2$ and $(H_L)_3$ values at a given Re within the limits of experimental error. The value of H_L decreases monotonically with boilup rate. The apparent convergence of the experimental curves at low boilup rate is now seen to be a result of the convergence of the constructed H_V lines at the origin.

If we assume that the reflux film was laminar at the lowest boilup rate of Q = 2,500 ml/hr. (Re_L =20), the liquid diffusivity is estimated from Westhaver theory to be $D_L = 8.0 \times 10^{-6}$ $cm^2/sec.$ This differs from a value of $D_L = 4.6 \times 10^{-5}$ $cm^2/sec.$ using the methods of Wilke (66).

We conclude on the basis of these experimental data that

i) at low boilup rates there is a substantial liquid phase resistance which diminishes as the boilup rate is increased.

ii) This resistance is a function of the boilup rate, and is independent of Ta.

iii)The liquid diffusivity is estimated to be $D_L = 8.0 \times 10^{-6}$ $cm^2/sec.$

These conclusions are based on assumptions A and B.

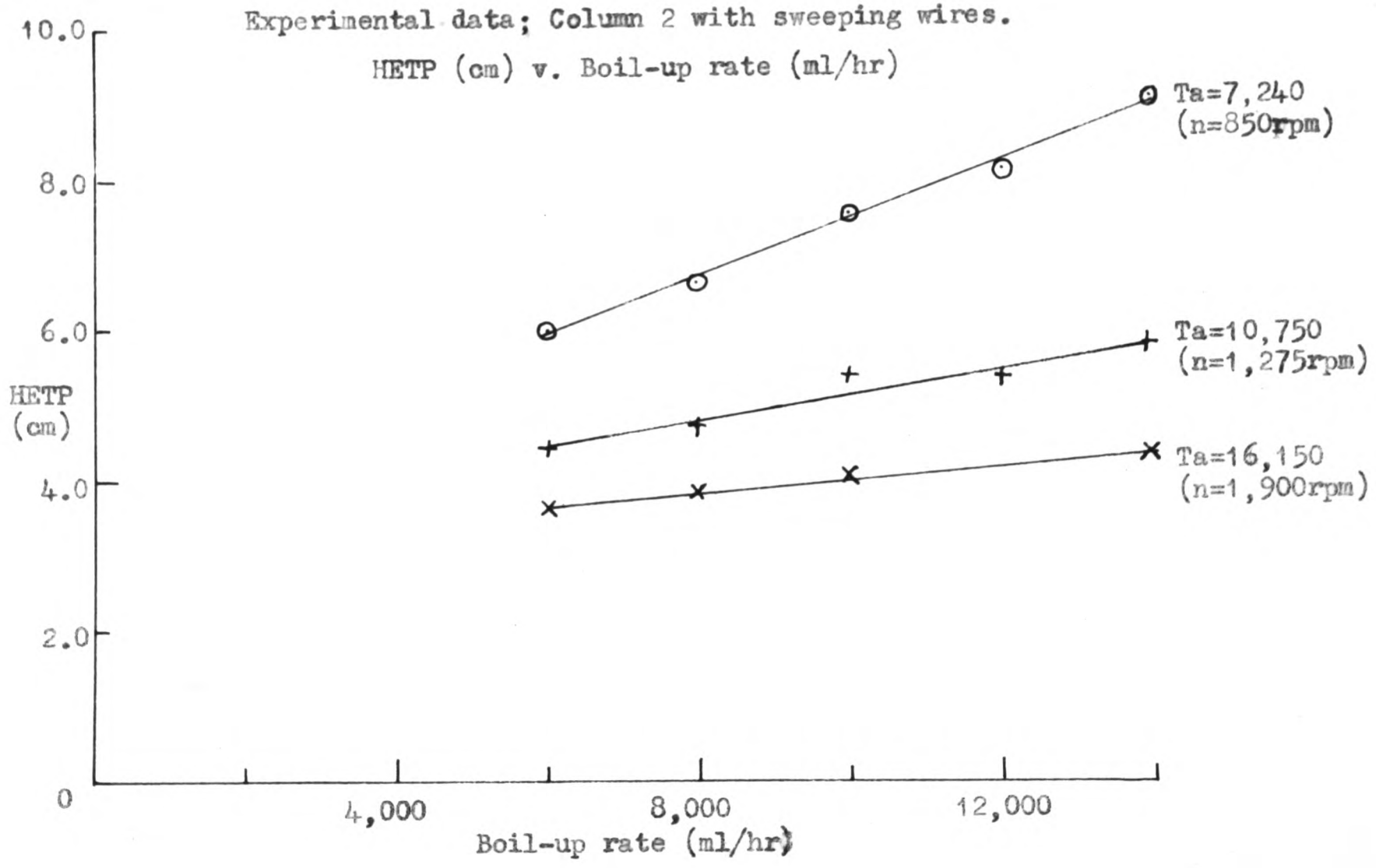
5.3.2 Experiments with sweeping wires

A set of experiments conducted under conditions similar to those just described was performed with sweeping wires attached to the rotor. A sixth assumption F may be made: no liquid-side resistance is present. In contrast with the findings in the absence of sweeping wires, it was not possible to obtain reproducible results at the two lowest boilup rates of Q = 2,500 ml/hr. and 4,000 ml/hr. Visual observation of the reflux at these wetting rates showed that with the wires in use the amount of reflux carried by a wire was sufficient to cause starvation on other parts of the stator/

FIG.5.4

Experimental data; Column 2 with sweeping wires.

HETP (cm) v. Boil-up rate (ml/hr)



stator surface. Results are plotted in Fig. 5.4 and are corrected for unstirred length of the stator. Stirring of the total stator length by the wires was not possible because of the method of attachment of the wires to the rotor. It was possible to estimate the wiped and unwiped lengths (by visual observation) as 70 cm. and 55 cm. respectively. Experiements were conducted at the end of this trial with the wires stirring the vapour only which confirmed there was no significant alteration in column performance due to the wire stirring the vapour. Comparison of Fig.s 5.1 and 5.4 show that:

i) Corresponding values of H are reduced to between $\frac{1}{2}$ and $^1/_4$ of their original values.

ii) At a given boilup rate H increases more rapidly than $Ta^{-0.5}$. Between Ta = 7,240 and Ta = 10,750, H varies more rapidly than $Ta^{-0.5}$ (i.e. the column performance increases more than would be expected from Westhaver/Shahbenderian/Flower theory on the basis of vapour phase controlling only), while between Ta = 10,750 and Ta = 16,150 there is roughly a square-root dependence between H and $(Ta)^{-0.5}$.

iii) The lines of H ~ Q for different values of Ta do not meet at the origin.

Neither of these last two observations is consistent with the assumptions A, B and F. It is most unlikely that F (no liquid side resistance) is incorrect for operating conditions with the sweeping wires. A reasonable hypothesis is that assumption A is false and the interfacial area is increased by the action of the wires. Observations of the swept reflux film described in section 4.2.9 of Chapter IV support this hypothesis. At Ta = 7,240, turbulent liquid was observed surrounding each wire, while at

Ta/

Ta = 10,750 fine bubbles were seen surrounding each wire. Increasing the rotor speed further caused this bubble entrainment to become more vigorous. It is therefore likely that assumption A is false for these operating conditions and the results of the sweeping wire experiments cannot be taken at their face value. At given Ta, the flatness of the curve shows that the interfacial area increases with boilup rate. In a simple qualitative sense this seems reasonable as at greater boilup rate there is more liquid film in which vapour can be entrained, and also there is more vapour (because of the greater vapour rate) available. Although Matterson observed no improvement in column performance for his distillation column at 1,470 rpm. (from which one may conclude that there was no liquid side resistance or interfacial area increase when the wires were used) his wires were moving at a lower speed, which probably was insufficient to cause appreciable surface area increase.

The alternative hypothesis is that assumption B - laminar + vortex flow in the vapour phase - is false. On this hypothesis the vapour flow is turbulent + vortex. The sweeping wire experiments are the only source of information about H_V and have to be taken at their face value. The improvement in separating power obtained with the wires is due to the abolition of a very large liquid-side resistance. If this is so, comparison of Fig. 5.3 and 5.4 shows that H_L increases with Re_L at constant Ta but decreases with increasing Ta at constant Re_L. This means that rotor windage is more effective in stirring the film than rippling. However, experimental and theoretical work previously referred to in Section 5.2.2 shows that rippling will substantially increase liquid phase mass transfer. On this basis, it is more likely that the hypothesis previously proposed, wherein H_L does not vary with Ta at constant/

constant Re_V, and reduces as Re_V increases at constant Ta, is correct, Also, as already suggested, it is highly probable that assumption A is invalid for the sweeping wire experiments and so they cannot be taken at their face value.

To conclude, then, hypothesis I, that of laminar + vortex vapour motion in the column with liquid phase resistance which decreases with increasing Re_V, provides an absolute estimate of the performance of column II in terms of the Westhaver/Shahbenderian/ Flower theory.

5.4 Experimental results Column I.

Experiments were conducted with the inner cylinder stationary and rotating. Preliminary experiments were conducted with n-heptane-methylcyclohexane as test-mixture. This mixture was later replaced with 2.2.4 trimethylpentane-methylcyclohexane for reasons given in Chapter IV.

During the operation of this column it was observed that boilup rates resulting from a given power input as measured by the rate-meter at the base of the column varied in spite of precautions taken to minimise draughts and prevent heat loss. Typically, a power input of 50 watts was necessary to maintain a boilup rate in the region of 500 ml/hr. Calculations, however, showed that only 30 watts were used to vaporize the mixture and 20 watts were lost. This means that the leat loss was comparable in size with the not power supplied to the test-mixture, so any small variation in ambient conditions affected the boilup rate appreciably. This is thou ght to be a principal cause of experimental scatter of the results obtained with this column.

On/

On two occasions where the column was reassembled, it was impossible to reach thermal equilibrium with the thermistor and thermocouple pairs as described in Chapter IV. Under such conditions, it was subsequently found that there was a net flow of heat radially into the column and abnormally low values of separating power were observed. After the first occurrence, this fault was cured by the insertion of a thermal resistance in the air gap between the copper jacket supporting the column and the outside wall of the stator. A later recurrence of this phenomenon was cured by replacing some of the asbestos thermal resistance which had not been inserted in the gap.

5.4.1 Results with stationary inner cylinder

With the n-heptane-methylcyclohexane mixture, results were obtained with a power input to the stillpot heater of 50 watts which corresponded to a boilup rate range of 460 - 500 ml/hr. The importance of boilup rate measurements as distinct from power input measurements was not realised at this stage and consequently only a few check determinations of the reflux return rate by boilup meter were made.

As no precautions were taken to ensure even reflux division between inner and outer cylinders results may be expected to fall between the limits predicted by the Westhaver equations for one and both walls wetted. Values of H varied from 2.74 cm. to 4.50 cm. when the column was preflooded. The limiting values predicted by the Westhaver equation were 3.28 - 9.8 cm. The best values of separating power were thus better than those predicted, assuming $D_V = 0.031\ cm^2/sec.$

The few remaining results which were obtained using 2.2.4 trimethylpentane/Methylcyclohexane do not contradict Westhaver theory assuming D_v = 0.029 cm^2/sec.

5.4.2 Further inferences from Westhaver-Shahbenderian theory with inner cylinder rotating.

In the absence of liquid-side resistance Inference IV predicts the effect of altering column dimensions. Under certain circumstances, if liquid side resistance is present in one column, altering the dimensions may alter the amount of the liquid side resistance for given Re_V and Ta. For example in Column II at the lowest boilup rate of Q = 2,500 ml/hr. which corresponds to Re_L = 20, there is a substantial liquid phase resistance found. Visual examination of the reflux stream at this wetting rate shows no evidence of rippling. This lack of rippling is confirmed by a prediction of Portalski. However, Matterson has shown that there is negligible liquid side resistance in Column I at similar values of Re_L (corresponding to Q = 600 ml/hr.), from his sweeping wire experiments. The effect of vapour drag on the liquid surface in Column II is thus negligible at Re_L = 20 but is appreciable in Column I causing mixing of the reflux film and consequent lowering of H_L. This reasoning can be extended as follows.

5.4.2.1/

5.4.2.1 Variation of H_L with column size.

In Column II we observe that H_L decreases as the boilup rate increases. This is in contradiction to simple Westhaver theory which predicts that:

$$H_L \propto Q^{4/3}$$

The observed relation is therefore due to the interaction of vapour and liquid streams which is by the shear stress τ at the interface. Consider the operation of columns 1 and 2 at Re_v=280 (Re_L=20). Under these conditions the respective boil-up rates will be: Q_1=600 , Q_2=2,500ml/hr. The Nusselt equation for the thickness of a falling liquid film in the absence of shear at the free surface:

$$w_L = \left(\frac{Q \nu_L}{2400 \pi r_0 g}\right)^{1/3}$$

shows that the respective reflux thicknesses would be approximately equal if the upward flow of vapour had no effect on the mean motion of the liquid. On this basis, at a given Re_L (and Re_v) the interfacial shear stress would act on films of approximately equal thickness.

At a given Re_v it is clear that the interfacial shear stress in Column 1 will be higher (as a result of the higher vapour velocity) than that in Column 2. It is possible that the effect on the motion of the reflux will be such that the value of H_L in the small column will be substantially reduced and the value in the large column be relatively unaffected.

It is reasonable to assume that, where the surface velocity of the liquid is very small compared with the mean vapour velocity, the interfacial shear, τ, can be taken to depend on ρ_v, μ_v, ν_v, b, r_0, and ω alone. Application of the π-thereom gives:

$$\frac{\tau}{\rho \nu_v^2} = f\left(Re_v, Ta, b/r_0\right)$$

As the comparison is between columns which are geometrically similar the term b/r_0 may be omitted. The pressure-drop data of Flower (22) have shown that the effect of changes of Ta on the interfacial shear stress is small when the gas flow regime is laminar+vortex. Hence:

$$\frac{\tau}{\rho \nu_v^2} = f(Re_v)$$

This accords with the experimental findings in Column 2 that H_L is

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independent of Ta, but varies with Re_v. On these provisional simplifying assumptions, comparison of shear stresses in columns 1 and 2 at the same Re_v gives:

$$\frac{\tau_1}{\tau_2} = \frac{u_1^2}{u_2^2}$$

but at the given Re_v, $u_1 b_1 = u_2 b_2$,

$$\therefore \frac{\tau_1}{\tau_2} = 17.2$$

Although the form of relation between H_L and τ is not known, it seems reasonable to suppose that the greater shear stress in Column 1 will have a greater effect in reducing H_L than it will in Column 2 at the same Re_v.

This hypothesis is consistent with the results of Matterson, who found no liquid-side resistance in Column 1 from his sweeping-wire experiments, and with the visual observations of Column 2 in the present study, which showed there was no rippling or disturbance of the liquid film attributable to the vapour flow at the same Re_v. A substantial liquid-side resistance may therefore be presumed to have been present in Column 2, at least under some conditions of operation. In the absence of liquid-side resistance in Column 1, HETP will vary inversely as the square root of rotor speed and directly with boil-up rate as predicted from Inference 1. Assumptions A and B are certainly correct for the operating conditions of Column 1.

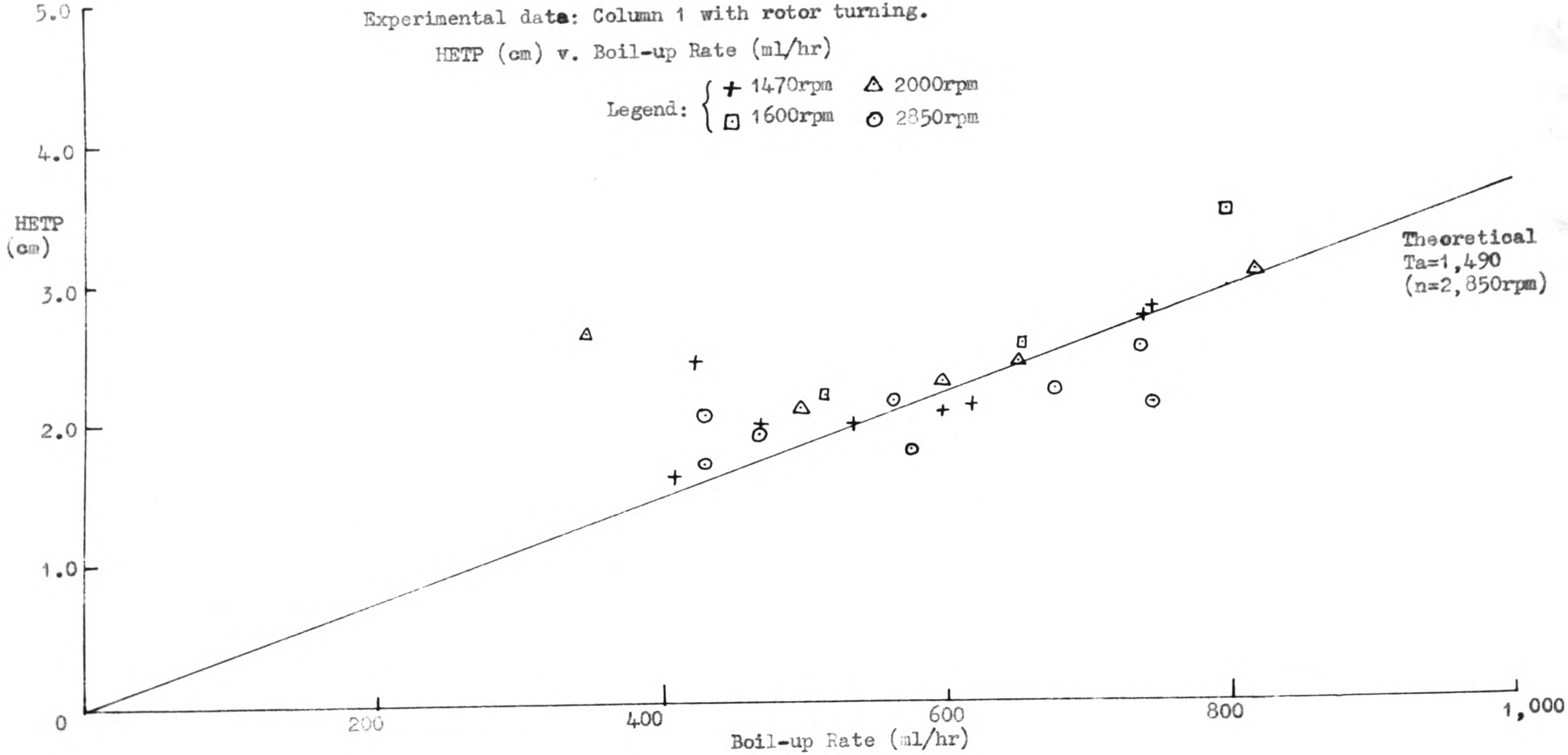
(2) p 104

FIG.5.6

Experimental data: Column 1 with rotor turning.

HETP (cm) v. Boil-up Rate (ml/hr)

Legend: + 1470rpm △ 2000rpm ⊡ 1600rpm ⊙ 2850rpm



5.4.3 Results for column I with inner cylinder rotating

For the majority of the initial experiments, which were conducted using n-heptane-methylcyclohexane, the jacket heaters were not correctly controlled by the thermistor and thermocouple pairs, and there was radial flow of heat into the column. All these experiments were conducted in the boilup rate range 550 - 650 ml/hr. at rotor speeds varying between 650 - 2,260 rpm. These corresponded to $230 < Re_V < 275$ and $340 < Ta < 1,180$ assuming $\nu_v = 0.031$ cm^2/sec. The scatter of these results was very large and was more than sufficient to mask any expected variation of H.E.T.P. with Ta.

Using 2.2.4 trimethylpentane methylcyclohexane test mixture values of separating power were obtained in the boilup range 250 - 850 ml/hr. and rotor speeds were varied between 670 - 2,850 rpm. Assuming $\nu_v = 0.031$ cm^2/sec these ranges correspond to $106 < Re < 360$ and $350 < Ta < 1,490$. Some of these results, including the majority of those at 670 rpm. rotor speed were obtained when there was radial heat flow into the column, as described above. Comparison of these with those obtained under adiabatic conditions, shows the scatter was reduced and values of separating power were higher for the latter condition.

Results obtained for adiabatic conditions are shown opposite in Fig. 5.6. In spite of the numerous minor improvements made to the column (such as supplying power from a constant-voltage transformer and controlling condenser coolant flow) which are described in detail in Chapter IV, the scatter is large. Much of this scatter can be attributed to the heat loss from the stillpot heater being comparable in magnitude with the net power input to the stillpot contents. The following points can be noted:

i)/

i) The scatter is much greater than was observed with column II.

ii) For a given Re_V there is no apparent dependence of H upon Ta.

iii) At the highest boilup rates, values of H at Ta = 1,490 are less (i.e. column performance is better) than predicted from column II on the basis of controlling vapour phase resistance.

It is doubtful whether the three results at Ta = 350 can be taken at their face value. Visual observation of the rotor using stroboscopic light showed its motion to be eccentric at n = 670 rpm. This eccentric motion was not apparent at higher rotor speeds of 1,470 - 2,850 rpm. It seems doubtful, therefore, whether the vapour motion at this low speed was laminar + vortex; there may well have been additional vapour mixing. The speeds of 1,470 and 2,850 rpm. were obtained using mains power supply, and they appeared constant. The other speeds of 670 and 2,000 rpm. were obtained with the variable frequency generator. This performed smoothly at the high speed (which gave regular and smooth running at n = 2,000 rpm.) but did not at the lowest speed.

The large scatter present in the remaining results is sufficient to mask the expected variation of $H \propto (Ta)^{-0.5}$. However, results at Ta = 1,490 are slightly better than predicted (i.e. H is less than predicted) while those at Ta = 770 are much better than predicted. This suggests either i) that the positions of the theoretical curves are incorrect or

ii) measured values of the boilup rate are too high.

5.4.4/

5.4.4 Heat loss from Column I

When thermal balance was attained between the thermistor and thermocouples in the lower and middle sections, it was seldom possible to get thermal balance in the top section. Although the heating jacket was in three sections, these sections heated a copper jacket which was able to conduct heat axially. If the supply of heat to the top section was increased, some of this additional heat was also supplied to the lower and middle sections, thereby destroying the thermal balance in these sections.

Measurement of liquid rates at the top and bottom of the column confirmed this heat loss. Typically, for a boilup rate of 500 ml/hr. as measured by the boilup meter at the bottom of the column, the distillate rate was only 50 ml/hr. This means that there was progressive condensation occurring in the top section of the column which will result in an abnormally high number of theoretical plates per unit length in this region. The following calculation will make this clear.

Let the distillation column operate as shown opposite, in Fig. 5.7. Let the number of theoretical plates in the adiabatic length l_A be N_A, and in the non adiabatic length l_B be N_B. In addition let the boilup rate at the bottom of the column be Q_L and at the top be Q_T.

Along the (non adiabatic) length l_B, the mean boilup rate

$$Q_M = \frac{Q_T + Q_L}{2}$$

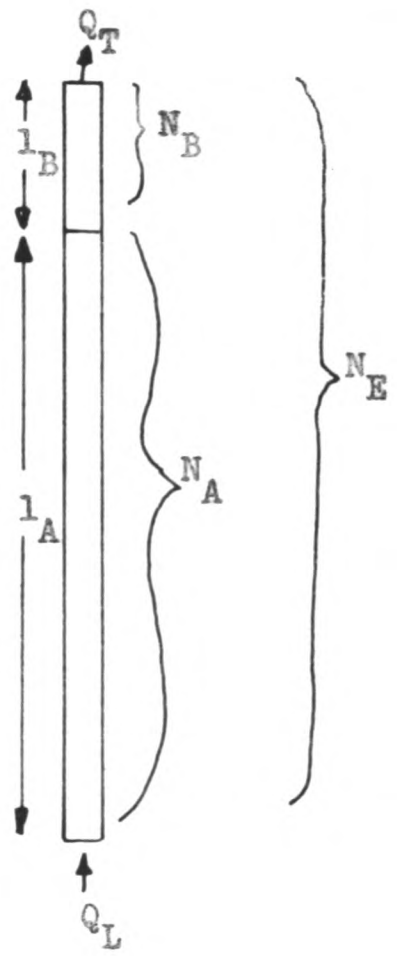
Also the measured separating power

$$N_E = N_A + N_B$$

and/

FIG.5.7

Heat loss effects in Column 1.



and the required separating power

$$N_C = N_A \frac{l_A + l_B}{l_A}$$

Consider a typical case

N_E = 30 plates, Q_L = 500 ml/hr, Q_T = 50 ml/hr.

now: $$\frac{N_B}{N_A} = \frac{l_B}{l_A} \frac{H_A}{H_B}$$

but $$\frac{H_A}{H_B} = \frac{Q_L}{Q_M}$$

$$\therefore \frac{N_B}{N_A} = \frac{l_B}{l_A} \frac{Q_L}{Q_M}$$

assume l_A = 50 cm., l_B = 10 cm.

$$\therefore N_B = N_A \frac{10}{50} \frac{500}{275} = 0.364\ N_A$$

but $N_E = N_A + N_B = 1.364\ N_A$

$$\therefore N_A = 22.0$$

hence $N_C = 22.0 \times \frac{60}{50}$

$= 26.4$ plates

This means the corrected value of H.E.T.P. will be H_V = 2.50 cm. instead of H_V = 2.00 cm. If the length over which condensation occurs is greater, naturally the corrected value of H will be even greater. For l_A = 40 cm. l_B = 20 cm. (which is the worst possible case for column I) the corrected value of H_V = 2.54 cm.

This calculation shows clearly that the measured values of H_V might well be greatly reduced below expectation because of this heat loss.

To/

To conclude, the results from column I are not in disagreement with the predictions of the Westhaver/Shahbenderian/Flower theory from column II when the following restrictions are noted:

i) The few results at low Ta (Ta = 350) are unreliable

ii) The scatter of the remaining results is great enough to mask the expected variation of H with Ta.

iii) The absolute values of H as measured are too low because of heat loss from the top of the column.

5.5 Results of Willingham et al.

The results of Willingham et al. (4) are shown in Fig. 2.6 and have been discussed in Chapter II. Accepting the values of H_V estimated from column II results, there is no liquid side resistance at Ta = 940 (n = 4,000). At Ta = 635, H_L is approximately constant ($H_L \sim 0.5$ cm.) over the boilup range, while at Ta = 400, liquid phase control predominates with H_V varying from $0.8 < H_V < 3.2$ cm. and $2.6 < H_L < 4.5$ cm. This variation of H_L with Ta and not with Re_V contradict the results from column II where H_L is constant with Ta and decreases with Re_L. From equation 5.7, u_V for this column is much greater than for column II at comparable Re_V so no liquid phase resistance would be expected. However, geometrical similarity is assumed in the analysis which is not the case here - for Willingham et al. $^{b}/_{r_o} = 0.029$ which is about 8 times less than the present $^{b}/_{r_o} = 0.231$. It is therefore possible that H_L will be a function of Ta rather than Re_V. Calculation of effective liquid diffusivity from the greatest $H_L = 4.5$ cm. at Q = 2,000 ml/hr., Ta = 400 gives $D_L = 8 \times 10^{-6}$ cm^2/sec. This is in close agreement with the value of D_L estimated from the present work when the liquid film was considered laminar. It seems strange, however/

however, that under the conditions Q = 2,000 ml/hr. and Ta = 400 for Willingham's column the liquid flow should be laminar bearing in mind the high vapour velocity. It is more likely that at low values of Ta (Ta $\leqslant$ 400) and boilup rate where the form of relation between H.E.T.P. and Re_V is different from that at higher Ta there was a basic fault in the operation of their column which gives rise to apparently high values of H_L, but there is no apparent reason why this should be so.

Chapter VI

6.1. Introduction

In Chapter I, the purposes of the general programme of work were stated to be:

a) to put the practical design of rotary concentric tube fractionating columns on a rational basis to enable the scope and limitations of this type of column to be assessed.

b) to examine the applicability (to this particular case) of general theories of mass transfer and distillation.

6.2. Results from the present investigation

The experimental findings of the present investigation have been compared with inferences drawn from the Westhaver/ Shahbenderian/Flower theory, which itself is based on classical steady-state mass transfer theory. This comparison has shown that the results are not in disagreement with these inferences and hence it is reasonable to suppose that general mass transfer theory is applicable in this particular case. Moreover, this comparison has helped to put the design of such columns on a rational basis.

6.3. Column 2 results

In particular, a significant liquid side resistance to mass transfer has been found to exist under operating conditions studied in Column 2. Attempts to determine values of H_L by comparison of column performance with the reflux stirred by sweeping wires (attached to the rotor) and normal reflux for corresponding Re_V and Ta were unsuccessful, apparently because one of the assumptions, namely that of constant interfacial area, was no longer true in this case; it is believed that the sweeping wires increased the interfacial area by an unknown amount.

However,/

However, it was possible to determine the relative proportions of H_V and H_L over the range of Re_V and Ta by graphical methods. The method used indicates that if the variation of H_V is as predicted from Westhaver/Shahbenderian/Flower theory, viz.: $H_V \propto (Ta)^{-0.5}$ and $H_V \propto Re_V$, assuming laminar + vortex flow regime in the annular gap, then H_L decreases with increasing Re_V and is substantially independent of Ta. This variation of liquid side conductances is not in disagreement with other mass transfer findings (61,63) with a rippling film of liquid.

6.4. Column 1 results.

There is good reason to suppose that liquid side resistance in the smaller distillation column was negligible over the range of conditions studied, both from experimental work performed by Matterson with and without reflux stirred by wires and from a dimensional analysis of this problem which shows the effect of vapour drag to be much greater in Column 1 than in Column 2. It is thus possible to predict values of H_V, and hence the separating power, for the small column from H_L values for Column 2 obtained from the graphical solution referred to in 6.3 by means of the dimensional predictions of the theory.

Apart from the very few results conducted at the lowest Ta which are suspect on account of the observed irregular motion at a rotor speed of 670 rpm., results from the small column show no dependence of H with Ta and some values of H_V are significantly lower (i.e. the separating power is better) than values predicted in themanner described above. However, the experimental scatter of these values is so large as to mask completely the expectation that $H \propto (Ta)^{-0.5}$ over the relevant range of operating conditions.

Moreover,/

Moreover, heat losses from the upper part of the column were appreciable, and as the calculation in 5.4.4 shows, could be sufficient to account for the apparent improvement on theory. Taking into account these peculiarities, it is most likely that these experimental values are not in disagreement with Westhaver/ Shahbenderian/Flower theory. The excessive scatter is a consequence of the heat loss from the stillpot being comparable with the net heat input to the pot contents.

6.5 Comparison of column 1 and Column 2 results

The principal difference between the results from the two columns is that a substantial liquid side resistance is present in column 2 which is entirely absent in column 1. For a given Re_v (and hence Re_L) the behaviour of the liquid film of reflux in Column 2 is approximately what would be expected in the absence of the upward motion of the vapour, while in column 1 for the same Re_v the effect of vapour motion is much greater. This is due to the much greater vapour velocity in the narrower gap: for a given Re_v, $u_v \propto (b)^{-1}$.

6.6. Practical uses of these columns

These columns are of interest in the separation of close boiling materials on account of their high separating power and very low holdup and pressure drop. Typical values of separating power for column 1 are of the order of 35 plates/metre at rotor speed of c. 3000 rpm. and boilup rate of 500 ml/hr, and for column 2 a separating power of c. 6 plates/metre at the highest rotor speed investigated at 1900 rpm. and boilup rate of 14,000 ml/hr. With the sweeping wires attached the separating power of column 2 is increased fourfold to 23 plates/metre for the same boilup rate and rotor speed. In addition, with the sweeping wires attached, the separating/

separating power is relatively insensitive to changes in boilup rate: thus at 6000 ml/hr (and 1900 rpm.) the separating power has risen to only 27 plates/metre, an increase of 15% compared with the drop in boilup rate to 50% of its original value. Because of the greatly enhanced performance owing to the presumed increase in interfacial area, it is therefore worth operating this column with sweeping wires attached to the rotor.

6.7. Suggestions for further work

6.7.1. Determination of physical properties

There is lack of information on physical properties of the test mixture used in the present investigation. Values of Ta, Re_v and Re_L are not accurately known because of the absence of reliable data on ν_L and ν_v, the liquid and vapour kinematic viscosities. In addition, it is not possible even to estimate with any degree of certainty values of vapour and liquid diffusivities, D_v and D_L (particularly the latter) from existing correlations because of the absence of data on physical properties. No values of D_v and D_L have been experimentally determined. It is therefore necessary to devise a programme of work to determine vapour and liquid densities and viscosities at the boiling point of the test-mixture. Values of Ta, Re_v and Re_L could then be accurately calculated. Variation of vapour viscosity with temperature could be used to determine the Lennard-Jones force constantss to provide a more reliable estimate of vapour diffusivity. Measurements of the velocity of sound in the liquid as described by Collins and Navidi (78) could then be used in Kamal's (67) method for estimating D_L. These estimated values of D_v and D_L should then be compared with experimentally determined values which are also required.

6.7.2./

6.7.2. Investigation of column performance under vacuum

Rotary concentric tube fractionating columns would appear attractive for separation at reduced pressure on account of their low pressure drop. However, as Zuiderweg (79) has shown for wetted wall columns H_V will remain relatively unchanged as the pressure is reduced for a given throughput while the liquid-side resistance H_L will increase. Moreover, the vapour-side resistance will be less affected by the Ta in the present rotary type of column at reduced pressure. It is thus worth investigating the altered dependence of H on the operating variables at reduced pressure, using similar boilup rates and rotor speeds already used in Column 2 in the present atmospheric work. Experiments with sweeping wires should also be conducted, to see whether there is an enhancement in column performance similar to that obtained at atmospheric pressure in the present work. A recommended test mixture, suggested in Chapter III is n-decane/transdecalin which at a convenient operating pressure of 100 mmHg has relative volatility $\alpha = 1.305$ and could therefore be used for columns with separating power of up to 20 theoretical plates, assuming stillpot and distillate compositions of 0.1 and 0.9 mole fraction of the more volatile component.

Appendix A.

Derivation of H.E.T.P. for the concentric tube distillation column; with one wall wetted and stationary inner cylinder. Shahbenderian, in Appendix C of his thesis, presented an expression for the H.E.T.P. for a concentric tube wetted-wall distillation column, when the annular gap is too large to permit use of the parallel plate approximation utilised by Westhaver in his simplified analysis.

The expression so obtained is:

$$H = \frac{\bar{u}_1 (r_w^2 - r_1^2)}{2DE^2} \int_{r_1}^{r_w} f(r)\, dr$$

where E is a constant which is dependent on the geometry of the system and $f(r)$ is a function of r, the tube radius. Although it is possible to integrate this function between the specified limits, Shahbenderian notes that this would be a lengthy and tedious procedure, and instead recommends using a numerical solution by means of a digital computer for any particular case required.

The full analysis of the problem is presented below, then the theoretical values of H.E.T.P. so calculated are compared with the values of H.E.T.P. using the parallel-plate approximation for a number of examples given in the literature.

Writing a mass balance on an element of vapour gives:

$$D \frac{\partial}{\partial r}\left(r \frac{\partial c_y}{\partial r}\right) + r D \frac{\partial^2 c_y}{\partial z^2} = r \frac{\partial u c_y}{\partial z} \qquad \text{(A1)}$$

Neglecting longitudinal diffusion and integrating

$$D r \frac{\partial c_y}{\partial r} = \int r \frac{\partial u c_y}{\partial z} + \phi \qquad \text{(A2)}$$

where ϕ is constant of integration.

The vapour velocity profile in an annular gap is given ( ):

$$u = -\frac{dp}{dz}\frac{1}{4\mu}\left[r_w^2 - r^2 + 2r_{max}^2 \ln\frac{r}{r_w}\right] \qquad (A3)$$

where $r_{max}^2 = \dfrac{r_1^2 - r_w^2}{2\ln\frac{r_1}{r_w}}$

and is the radius at which the maximum velocity occurs.

Substituting the expression for the velocity (A3) in (A2):

$$\partial r\frac{\partial cy}{\partial r} = c\frac{\partial y}{\partial z}\int\frac{dp}{dz}\frac{1}{4\mu}\left\{r_w^2 r + 2r_{max}^2\left[r\ln r - r\ln r_w\right]\right\}dr + \phi$$

$$= c\frac{\partial y}{\partial z}\frac{dp}{dz}\cdot\frac{1}{4\mu}\left\{\frac{r_w^2 r^2}{2} + 2r_{max}^2\left\{\frac{r^2}{2}\left(\ln\frac{r}{r_w} - \frac{1}{2}\right)\right\} - \frac{r^4}{4}\right\} + \phi \qquad (A4)$$

At the inner wall $r = r_1$, $\left(\dfrac{\partial cy}{\partial r}\right)_{r=r_1} = 0$

$$\phi = -c\frac{\partial y}{\partial z}\cdot\frac{dp}{dz}\cdot\frac{1}{4\mu}\left\{\frac{r_w^2 r_1^2}{2} + r_{max}^2 r_1^2\left(\ln\frac{r_1}{r_w} - \frac{1}{2}\right) - \frac{r_1^4}{4}\right\} \qquad (A6)$$

Integrating (A4) gives:

$$y = \frac{1}{D}\frac{\partial y}{\partial z}\cdot\frac{dp}{dz}\cdot\frac{1}{4\mu}\left\{\frac{r_w^2 r^2}{4} + \frac{r_{max}^2}{2}r^2\left(\ln\frac{r}{r_w} - 1\right) - \frac{r^4}{16}\right\} + \frac{\phi\ln r}{Dc} + \frac{\psi}{Dc} \qquad (A7)$$

At the interface, $y = y_1$, $r = r_w$:

$$\therefore\quad y = y_1 + \frac{1}{D}\frac{\partial y}{\partial z}\cdot\frac{dp}{dz}\cdot\frac{1}{4\mu}\left\{g(r) - g(r)_w\right\} + \frac{\phi}{Dc}\cdot\ln\frac{r}{r_w} \qquad (A8)$$

where $g(r) = \dfrac{r_w^2 r^2}{4} + \dfrac{r_{max}^2}{2}r^2\left(\ln\dfrac{r}{r_w} - 1\right) - \dfrac{r^4}{16}$

$$g(r)_w = \frac{3r_w^4}{16} - \frac{r_{max}^2 r_w^2}{2}$$

The elemental volume flow dV

$$dV = u\,2\pi r\,dr$$

$$\therefore\quad V = \int 2\pi u r\,dr$$

$$\therefore\quad \bar{u} = \frac{\int_{r_1}^{r_w} 2\pi u r\,dr}{\pi\left(r_w^2 - r_1^2\right)}$$

Substituting the value for u from equation (A3) and integrating:

$$\bar{u}_1 = \frac{2}{(r_w^2 - r_1^2)} \frac{dp}{dz} \cdot \frac{1}{4\mu} \cdot E$$

where:

$$E = \left\{ \frac{r_w^4}{4} + \frac{r_1^4}{4} - \frac{r_w^2 r_1^2}{2} + r_{max}^2 \left(\frac{r_1^2}{2} - \frac{r_w^2}{2} - r_1^2 \ln \frac{r_1}{r_w} \right) \right\} \qquad \text{(A9)}$$

$$\frac{1}{4\mu} \frac{dp}{dz} = \frac{(r_w^2 - r_1^2)\,\bar{u}_1}{2E} \qquad \text{(A10)}$$

Recapitulating equation (A1) and neglecting longitudinal diffusion as before:

$$\mathcal{D} \frac{\partial}{\partial r}\left(r \frac{\partial cy}{\partial r}\right) = r\left(\frac{\partial cuy}{\partial z}\right)$$

Integrating and inserting limits:

$$\mathcal{D}\left(r \frac{\partial cy}{\partial r}\right)_{r=r_w} = \int_{r_1}^{r_w} r \frac{\partial}{\partial z}(cuy)\, dr \qquad \text{(A11)}$$

assuming $\left(\frac{\partial cy}{\partial r}\right)_{r=r_1} = 0$

Now define a mass transfer coefficient K, such that

$$K = \frac{\mathcal{D}\left(\frac{\partial cy}{\partial r}\right)_{r=r_w}}{(\bar{y}_1 - \bar{y})} \qquad \text{(A12)}$$

where y_1 is the value of y at the interface

and $$\bar{y} = \frac{1}{\bar{u}\,\pi(r_w^2 - r_1^2)} \int_{r_1}^{r_w} 2\pi u y r\, dr \qquad \text{(A13)}$$

The total molal flow, V, is:

$$V = \bar{u}\, c\, \pi (r_w^2 - r_1^2) \qquad \text{(A14)}$$

Combining (A13) and (A14) gives:

$$V\bar{y} = c \int_{r_1}^{r_w} 2\pi u y r\, dr \qquad \text{(A15)}$$

and differentiating

$$\frac{d}{dz}(V\bar{y}) = \int_{r_1}^{r_w} 2\pi r \frac{\partial}{\partial z}(cuy) \cdot dr$$

and substituting (A11) and (A13):

$$\frac{d}{dz}(V\bar{y}) = 2\pi K r_w (y_1 - \bar{y}) \qquad \text{(A16)}$$

Writing a mass balance across any section of the column

$$(V\bar{y}) = L\bar{x} + \pi (r_w^2 - r_1^2) \, D \, \frac{d}{dz} c\bar{y}' \qquad \text{(A17)}$$

where $$\bar{y}' = \frac{1}{\pi(r_w^2 - r_1^2)} \int_{r_1}^{r_w} 2\pi r y \, dr$$

Assuming $\bar{y} = \bar{y}'$ and differentiating (A17) w.r.t. z :

$$\frac{\partial}{\partial z}(V\bar{y}) = \frac{\partial}{\partial z}(L\bar{x}) = 2\pi K r_w (y_1 - \bar{y}) \qquad \text{(A18)}$$

assuming $D \frac{\partial^2 c\bar{y}'}{\partial z^2}$ negligible.

From (A17): $$\bar{y} = \frac{L}{V}\bar{x} = \frac{\pi (r_w^2 + r_1^2) \, D}{V} \frac{dc\bar{y}}{dz}$$

and substituting in (A18)

$$V \frac{d\bar{y}}{dz} = L \frac{d\bar{x}}{dz} = 2\pi r_w K \left\{ y_1 - \frac{L}{V}\bar{x} - \frac{\pi}{V}(r_w^2 - r_1^2) \, D \, \frac{d(c\bar{y})}{dz} \right\}$$

Rearranging gives:

$$\frac{d\bar{x}}{dz} \left\{ \frac{V}{2\pi r_w K} + \frac{D\pi (r_w^2 - r_1^2) c}{V} \right\} = \frac{V y_1}{L} - \bar{x} \qquad \text{(A19)}$$

Separating variables and integrating:

$$\frac{d\bar{x}}{dz} \left\{ \frac{V}{} \right. \qquad \int_{\bar{x}_0}^{\bar{x}_1} \frac{d\bar{x}}{\left(\frac{K}{L} y_1 - \bar{x}\right)} = \frac{\ell}{\left\{ \frac{V}{2\pi r_w K} + \frac{D}{u} \right\}} \qquad \text{(A20)}$$

which is analogous with $(NTU) = \frac{\ell}{(HTU)}$

or, assuming (HTU) = (HETP)

$$\text{then H.E.T.P.} = \left\{ \frac{V}{2\pi r_w K} + \frac{D}{u} \right\}$$

$$\approx \frac{V}{2\pi r_w K}$$ neglecting longitudinal diffusion.

$$\therefore \quad H = \frac{\bar{u} \, c (r_w^2 - r_1^2)}{2 K r_w} \qquad \text{(A21)}$$

K was earlier defined by equation (A12):

$$K = \frac{D\left(\frac{\partial \omega}{\partial r}\right)_{r=r_w}}{y_1 - \bar{y}}$$

By putting $r = r_w$ in equation (A4), the numerator of this equation is:

$$D\left(\frac{\partial \omega}{\partial r}\right)_{r=r_w} = c \frac{dy}{dz} \cdot \frac{dp}{dz} \cdot \frac{1}{4\mu} \left\{ \frac{r_w^3}{4} - \frac{r_{max}^2 r_w}{2} - \frac{M}{r_w} \right\}$$

where $$M = \frac{r_w^2 r_1^2}{2} + r_{max}^2 r_1^2 \left(\ln \frac{r_1}{r_w} - \frac{1}{2} \right) - \frac{r_1^4}{4}$$

Similarly, y is given in equation (A8):

$$y = y_1 + \frac{1}{D} \frac{dp}{dz} \cdot \frac{\partial y}{\partial z} \cdot \frac{1}{4\mu} \cdot B \qquad \text{(A22)}$$

where $$B = g(r) - g(r)_w - M \ln \frac{r}{r_w}$$

Now $$\bar{y} = \frac{1}{\bar{u}(r_w^2 - r_1^2)} \int_{r_1}^{r_w} 2ryu\,dr \qquad \text{(A13)}$$

Substituting the function of y (A21) gives:

$$\bar{y} = y_1 + \frac{2}{\bar{u}_1(r_w^2 - r_1^2)} \left(\frac{dp}{dz} \cdot \frac{\partial y}{\partial z} \frac{1}{4\mu} \right)^2 \frac{1}{D} \int_{r_1}^{r_w} r \cdot F(r) \cdot B(r)\,dr \qquad \text{(A23)}$$

where $$F(r) \frac{dp}{dz} \cdot \frac{\partial p}{\partial z} \cdot \frac{1}{4\mu} = u$$

$$\therefore \quad \bar{y} - y_1 = \frac{\bar{u}_1 (r_w^2 - r_1^2)}{2DE^2} \cdot \frac{\partial y}{\partial z} \int_{r_1}^{r_w} r \cdot F(r) \cdot B(r) \cdot dr$$

which is the denominator of the function for K.

Substituting in equation (A21) and rearranging gives:

$$H = - \frac{\bar{u}_1 (r_w^2 - r_1^2)}{2DE^2} \int_{r_1}^{r_w} r \cdot F(r) \cdot B(r) \cdot dr$$

which is identical with the expression obtained by Shahbenderian, except $B \equiv \int_{r_1}^{r_w} B(r) \cdot F(r) \cdot r \cdot dr$

The negative sign appears as Shahbenderian in his analysis dropped it in the algebra.

Various values of H were evaluated for distillation columns described in the literature, and compared with the values obtained using the parallel plate approximation. Values were obtained by numerical integration of the function by Simpson's rule using a Sirius computer: the accuracy required could be specified by the programmer. In all cases, the correct values of H.E.T.P. were lower than those predicted by the simpler method. Table AI below shows the divergence of the correct and simplified calculations for certain authors.

Table AI

Author	r_1 (cm)	r_0 (cm)	b/r_0	$\frac{H_s - H_c}{H_c}$ (%age)
Present construction	1.1	1.4	0.212	8.6
Donnel and Kennedy	0.62	0.70	0.114	3.5
Naragon and Lewis	0.33	0.4	0.175	6.8
Hall and Palkin	0.5	0.65	0.231	9.2
Shahbenderian	1.3	1.4	0.071	0.8
Naragon Burk et al.	0.5	0.6	0.167	6.2

Appendix B

Percentage error in the determination of the number of theoretical plates in a distillation column at total reflux

The number of theoretical plates, N, in a distillation column is often determined by the Fenske equation on the assumption that the mixture is ideal with a constant relative volatility:

$$N = \frac{\ln \frac{x_D(1-x_S)}{x_S(1-x_D)}}{\ln \alpha} - 1 \qquad \text{(B.1)}$$

Assuming that a small constant error is made in the measurement of refractive index or density it has been shown (29) that for a given number of plates (fixed N) using a particular test mixture (constant α) the error in N is least when the stillpot concentration x_S is as far below 0.5 as the distillate concentration is above 0.5, i.e.:

$$x_D + x_S = 1$$

This condition, while true, gives no indication of how the minimum value of the error in N varies with the actual value of N. The analysis is here extended to determine the variation of percentage error with the value of N, then proceeds to find the values of x_S and x_D, which give the true minimum values. Cases which are considered are for the test mixtures n-heptane-methylcyclohexane (α = 1.075) and 2,2,4 trimethylpentane (α = 1.049). Cases for determination of mole fraction by both density and refractive index are considered.

Neglecting 2nd order terms the error in determining the number of plates δN, is:

$$\delta N = \frac{\partial N}{\partial x_D} \cdot dx_D + \frac{\partial N}{\partial x_S} \cdot dx_S \qquad \text{(B.2)}$$

Assuming constant relative volatility and differentiating equation (B.1) with respect to x_D and x_S :

$$\frac{\partial N}{\partial x_D} = \frac{1}{\ln \alpha} \frac{1}{x_D(1-x_D)} \qquad (B.3)$$

$$\frac{\partial N}{\partial x_S} = \frac{1}{\ln \alpha} \frac{1}{x_S(1-x_S)} \qquad (B.4)$$

Substituting in equation (B.2) gives:

$$\delta N = \frac{1}{\ln \alpha} \left\{ \frac{dx_D}{x_D(1-x_D)} - \frac{dx_S}{x_S(1-x_S)} \right\} \qquad (B.5)$$

Case 1. The linear case.

The values of x_D and x_S are usually determined by a convenient analytical method, such as measurement of refractive index or density. In the simples possible case, a linear variation of mole fraction with the magnitude of the property is assumed:

$$i.e. \quad \rho = Ax + B \qquad (B.6)$$

$$\therefore \frac{d\rho}{dx} = A \qquad (B.7)$$

where A and B are constants, dependent on the system.

Since $$\frac{d\rho}{dx} \approx \frac{\delta \rho}{\delta x}$$

it follows that

$$\frac{\delta \rho_D}{dx} = A dx_D \qquad (B.8)$$

$$\delta \rho_S = A dx_S \qquad (B.9)$$

For a distillation column operating with a given separating power (i.e. particular N) it is possible to choose a value of x_S so that the percentage error in N consequent upon a given error in the measurement of P will be a minimum.

Let this error in the property measurement be δP .

For the worst possible case:

$$\delta P = |\, d\rho_D |$$

$$\delta P = |\, d\rho_S |$$

or expressed slightly differently:

$$d\rho_D = +\delta P \qquad \text{(B.10)}$$

$$d\rho_S = -\delta P \qquad \text{(B.11)}$$

Substituting in equation (B.5),

$$\delta N = \frac{\delta P}{A \ln \alpha} \left\{ \frac{1}{x_D(1-x_D)} + \frac{1}{x_S(1-x_S)} \right\} \qquad \text{(B.12)}$$

A function of the percentage error, E, may now be defined:

$$E = \frac{\delta N}{N} \cdot \frac{A}{\delta P} \qquad \text{(B.13)}$$

$$\therefore E = \frac{\dfrac{1}{x_D(1-x_D)} + \dfrac{1}{x_S(1-x_S)}}{\ln \dfrac{x_D(1-x_S)}{\alpha x_S(1-x_D)}} \qquad \text{(B.14)}$$

Since N is fixed, the expression for E contains one independent variable, x_S :

$$\frac{dE}{dx_S} = \frac{dE}{dx_D} \cdot \frac{dx_D}{dx_S} + \frac{dE}{dx_S}$$

Differentiating E with respect to x_S :

$$\frac{dE}{dx_S} = \left\{ \frac{(2x_D - 1)}{x_D^2(1-x_D)^2} \cdot \frac{x_D^2}{x_S^2 \alpha^{N+1}} + \frac{(2x_S - 1)}{x_S^2(1-x_S)^2} \right\} \div \left\{ \ln \frac{x_D(1-x_S)}{\alpha x_S(1-x_D)} \right\}$$

$$- \left\{ \frac{1}{x_D(1-x_D)} + \frac{1}{x_S(1-x_S)} \right\} \left\{ \frac{1}{x_D(1-x_D)} \cdot \frac{x_D^2}{x_S^2 \alpha^{N+1}} - \frac{1}{x_S(1-x_S)} \right\} \div \left\{ \ln \frac{x_D(1-x_S)}{\alpha x_S(1-x_D)} \right\}^2$$

(B.15)

At a maximum or minimum: $\dfrac{dE}{dx_S} = 0$

$$\therefore \left\{ \frac{(2x_D - 1)}{(1-x_D)^2} \cdot \frac{1}{x_S^2 \alpha^{N+1}} + \frac{(2x_S - 1)}{x_S^2(1-x_S)^2} \right\} N \ln \alpha$$

$$= \left\{ \frac{1}{x_D(1-x_D)} + \frac{1}{x_S(1-x_S)} \right\} \cdot \left\{ \frac{x_D}{(1-x_D)} \cdot \frac{1}{x_S^2 \alpha^{N+1}} - \frac{1}{x_S(1-x_S)} \right\} \qquad \text{(B.16)}$$

Numerical solution using a Sirius computer shows that the value of x_s to result in the minimum error using a particular test mixture to effect a particular separation is :

$$x_D + x_S = 1 \qquad \text{(B.17)}$$

The stillpot concentration should therefore be chosen such that it is as far below 0.5 as the distillate is above 0.5. This condition is true no matter what test mixture is chosen, i.e. independent of the value of α, although the magnitude of the error will not be the same for different test mixtures. Calculated values of the percentage error ($\delta N/N$) are given in tables I and II at the end of this Appendix.

Case 2. The quadratic case.

This case is more realistic than the simplified analysis given above. Both the test mixtures under consideration show a quadratic variation of mole fraction with refractive index.

We now have:

$$p = Ax^2 + Bx + C \qquad \text{(B.18)}$$

differentiating :

$$dp_D = (2Ax_D + B)\, dx_D$$

$$dp_S = (2Ax_S + B)\, dx_S$$

$$\therefore dx_D = \frac{dp_D}{(2Ax_D + B)} \qquad \text{(B.19)}$$

$$\therefore dx_S = \frac{dp_S}{(2Ax_S + B)} \qquad \text{(B.20)}$$

As in case 1,

$$dp_D = +\delta P$$
$$dp_S = -\delta P$$

$$\therefore \delta N = \frac{\delta P}{N \ln \alpha} \left\{ \frac{1}{x_D(1-x_D)(2Ax_D+B)} + \frac{1}{x_S(1-x_S)(2Ax_S+B)} \right\}$$

$$F = \frac{\dfrac{1}{x_D(1-x_D)(2Ax_D+B)} + \dfrac{1}{x_S(1-x_S)(2Ax_S+B)}}{\ln \dfrac{x_D(1-x_S)}{\alpha x_S(1-x_D)}} \qquad \text{(B.21)}$$

where $F = \left(\frac{\delta N}{N}\right) \cdot \frac{1}{\delta P}$

As before, to find the minimum value of F for a particular value of N, differentiate F with respect to x_s, and put equal to zero: $\frac{dF}{dx_s} \equiv \frac{dF}{dx_D} \cdot \frac{dx_D}{dx_s} + \frac{dF}{dx_s}$

Differentiating equation (B.21):

$$\frac{dF}{dx_s} = \left[\frac{6Ax_D^2 - (4A-2B)x_D - B}{x_D^2(1-x_D)^2(2Ax_D+B)^2} \cdot \frac{x_D^2}{x_s^2 \alpha^{N+1}} \cdot \ln \frac{x_D(1-x_s)}{\alpha x_s(1-x_D)} \right.$$

$$- \left\{ \frac{1}{x_D(1-x_D)(2Ax_D+B)} + \frac{1}{x_s(1-x_s)(2Ax_s+B)} \right\} \frac{x_D}{x_s^2(1-x_D)\alpha^{N+1}}$$

$$+ \frac{6Ax_s^2 - (4A-2B)x_s - B}{x_s^2(1-x_s)^2(2Ax_s+B)^2} \ln \frac{x_D(1-x_s)}{\alpha x_s(1-x_D)}$$

$$\left. + \left\{ \frac{1}{x_D(1-x_D)(2Ax_D+B)} + \frac{1}{x_s(1-x_s)(2Ax_s+B)} \right\} \frac{1}{x_s(1-x_s)} \right]$$

$$\div \left[\ln \frac{x_D(1-x_s)}{\alpha x_s(1-x_D)} \right]^2 \qquad (B.22)$$

Minimum values of $(\delta N/N)$ have been calculated for various values of N for the test mixtures n-heptane-methylcyclohexane and for 2,2,4 trimethylpentane-methylcyclohexane, and are tabulated in Tables III and IV at the end of this Appendix. These values were calculated by means of an Autocode programme for use with the Sirius computer, which is shown in Block diagram form after the tables at the end of this Appendix.

The calculated values are shown in Figs. 3.1 and 3.2, reproduced opposite for convenience. Two facts are immediately obvious:

(i) The difference in minimum error for the n-heptane test mixture, assuming linear, then quadratic dependence, is negligible, while for the 2,2,4 trimethylpentane mixture, it is noticeable, even though the simplification of the problem to the linear case, does not result in large changes of error at higher values of N.

It is also to be observed for the quadratic case, the criterion

$$x_D + x_s = 1$$

is no longer true, but becomes

$$x_D + x_s = A'$$

where A' is a fraction which appears to tend to a limiting value of unity as N is increased.

(ii) The tabulated values of N and $\left(\delta N/N\right)$, show that there is a minimum value of $\left(\delta N/N\right)$ reached. When N is further increased, the magnitude starts increasing very slowly.

It will now be shown by differentiation, that this is true.

Linear case.

Recapitulating, we have:

$$E = \frac{\frac{1}{x_D(1-x_D)} + \frac{1}{x_s(1-x_s)}}{\ln \frac{x_D(1-x_s)}{\alpha x_s(1-x_D)}} \qquad (B.14)$$

Since N is no longer fixed, we how have two independent variables x_D and x_s.

Differentiating with respect to x_D and x_s gives:

$$\frac{\partial E}{\partial x_D} = \left[\frac{(2x_D-1)}{x_D^2(1-x_D)^2} \ln \frac{x_D(1-x_s)}{\alpha x_s(1-x_D)} - \frac{1}{x_D(1-x_D)}\left\{\frac{1}{x_D(1-x_D)} + \frac{1}{x_s(1-x_s)}\right]\right] \div \left[\ln \frac{x_D(1-x_s)}{\alpha x_s(1-x_D)}\right]^2$$

$$\frac{\partial E}{\partial x_s} = \left[\frac{(2x_s-1)}{x_s^2(1-x_s)^2} \ln \frac{x_D(1-x_s)}{\alpha x_s(1-x_D)} + \frac{1}{x_s(1-x_s)}\left\{\frac{1}{x_D(1-x_D)} + \frac{1}{x_s(1-x_s)}\right]\right] \div \left[\ln \frac{x_D(1-x_s)}{\alpha x_s(1-x_D)}\right]^2 \qquad (B.23)$$

(B.24)

At a maximum or minimum

$$\left.\begin{aligned} \frac{\partial E}{\partial x_D} &= 0 \\ \frac{\partial E}{\partial x_S} &= 0 \end{aligned}\right\}$$

Adding (B.23) to (B.24), gives

$$\frac{(2x_D - 1)}{x_D(1-x_D)} = -\frac{(2x_S - 1)}{x_S(1-x_S)}$$

which has a solution

$$x_D + x_S = 1 \qquad \text{(B.17)}$$

Substitution of (B.17) in (B.23), gives:

$$(2x_D - 1)\left\{2 \ln \frac{x_D}{1-x_D} - \ln \alpha\right\} = 2$$

For n-heptane-methylcyclohexane, then

$$\alpha = 1.075 \qquad x_D = 0.827$$

$$x_S = 0.173$$

and for 2,2,4 trimethylpentane-methylcyclohexane:

$$\alpha = 1.049 \qquad x_D = 0.826$$

$$x_S = 0.174$$

Numerical calculation using the Fenske equation gives results in close agreement with these figures, and shows the shape of the surface to be a long shallow trough with a slight dip in the region of interest : over the range of values

$$0.10 < x_S < 0.20$$

$$0.95 > x_D > 0.85$$

the error changes by only a small amount.

Quadratic case.

Similar, though considerably more involved, calculations show that similar minima occur in the two quadratic cases considered;

These occur at

$x_D = 0.806$ for n-heptane methylcyclohexane

$x_S = 0.155$ ($\alpha = 1.075$)

and at

$x_D = 0.793$ for 2,2,4 trimethylpentane-

$x_S = 0.149$ methylcyclohexane ($\alpha = 1.049$)

In both these cases, the functional relations are given by Willingham et al. (43) for determining the mole fraction from the refractive index data.

Table B I

Linear dependent : n-heptane-methylcyclohexane (α = 1.075)

N	x_D	x_s	$\frac{\delta N}{N}$
6	0.563	0.437	7.80
8	0.581	0.420	5.89
10	0.598	0.402	4.78
12	0.616	0.385	3.72
14	0.633	0.368	3.52
16	0.666	0.335	3.22
20	0.681	0.319	2.62
22	0.696	0.303	2.48
24	0.712	0.288	2.34
26	0.727	0.274	2.22
28	0.740	0.260	2.14
30	0.754	0.246	2.07
32	0.768	0.232	2.02
34	0.780	0.220	1.97
36	0.792	0.208	1.93
38	0.804	0.196	1.92
40	0.815	0.185	1.90
44	0.836	0.164	1.90
50	0.863	0.137	1.95
54	0.879	0.120	2.01

The percentage error ($\delta N/N$) is computed using values of

$\delta p = 1.5 \times 10^{-4}$ A = 0.036.

Table B II

Linear dependent : 2,2,4 trimethylpentane-methylcyclohexane

(α = 1.049)

N	x_d	x_s	$\frac{\delta N}{N}$
10	0.565	0.435	3.99
12	0.577	0.423	3.34
14	0.588	0.412	2.89
16	0.600	0.400	2.56
18	0.611	0.389	2.30
20	0.623	0.377	2.08
22	0.634	0.366	1.92
24	0.645	0.355	1.78
26	0.656	0.344	1.67
28	0.666	0.334	1.58
30	0.677	0.323	1.49
34	0.697	0.303	1.36
38	0.717	0.283	1.27
42	0.736	0.264	1.20
46	0.754	0.246	1.15
50	0.771	0.229	1.11
54	0.788	0.212	1.09
60	0.811	0.189	1.06
65	0.828	0.172	1.06
70	0.845	0.155	1.07

The percentage error ($\delta N/N$) is computed using values of

$\delta p = 0.75 \times 10^{-4}$ A = 0.032

Table B III

Quadratic dependent : n-heptane-methylcyclohexane (α = 1.075)

N	x_D	x_s	$\frac{\delta N}{N}$
10	0.565	0.370	4.86
12	0.583	0.353	4.11
14	0.601	0.337	3.58
16	0.618	0.321	3.20
18	0.634	0.303	2.92
20	0.651	0.290	2.69
22	0.668	0.276	2.51
24	0.683	0.261	2.38
26	0.699	0.241	2.26
28	0.713	0.234	2.18
30	0.729	0.222	2.11
32	0.742	0.209	2.05
34	0.756	0.198	2.01
36	0.770	0.187	1.98
38	0.782	0.176	1.96
42	0.806	0.156	1.94
46	0.827	0.138	1.95
50	0.846	0.121	1.99
54	0.865	0.107	2.06
58	0.881	0.094	2.14

The percentage error ($\delta N/N$) is computed from values of $\delta p = 1.5 \times 10^{-4}$, A = 4.8, B = - 40.2; the values of A and B are taken from the functional relationship $n_D^{25} - 1.3851 = 0.0306 + 0.0048\,(x')^2$ given by Willingham et al (43) for the analysis by refractive index where n_D^{25} = R.I. at 25°C x' = mole fraction of methylcyclohexane.

Table B IV

Quadratic dependent : 2,2,4 trimethylpentane-methylcyclohexane

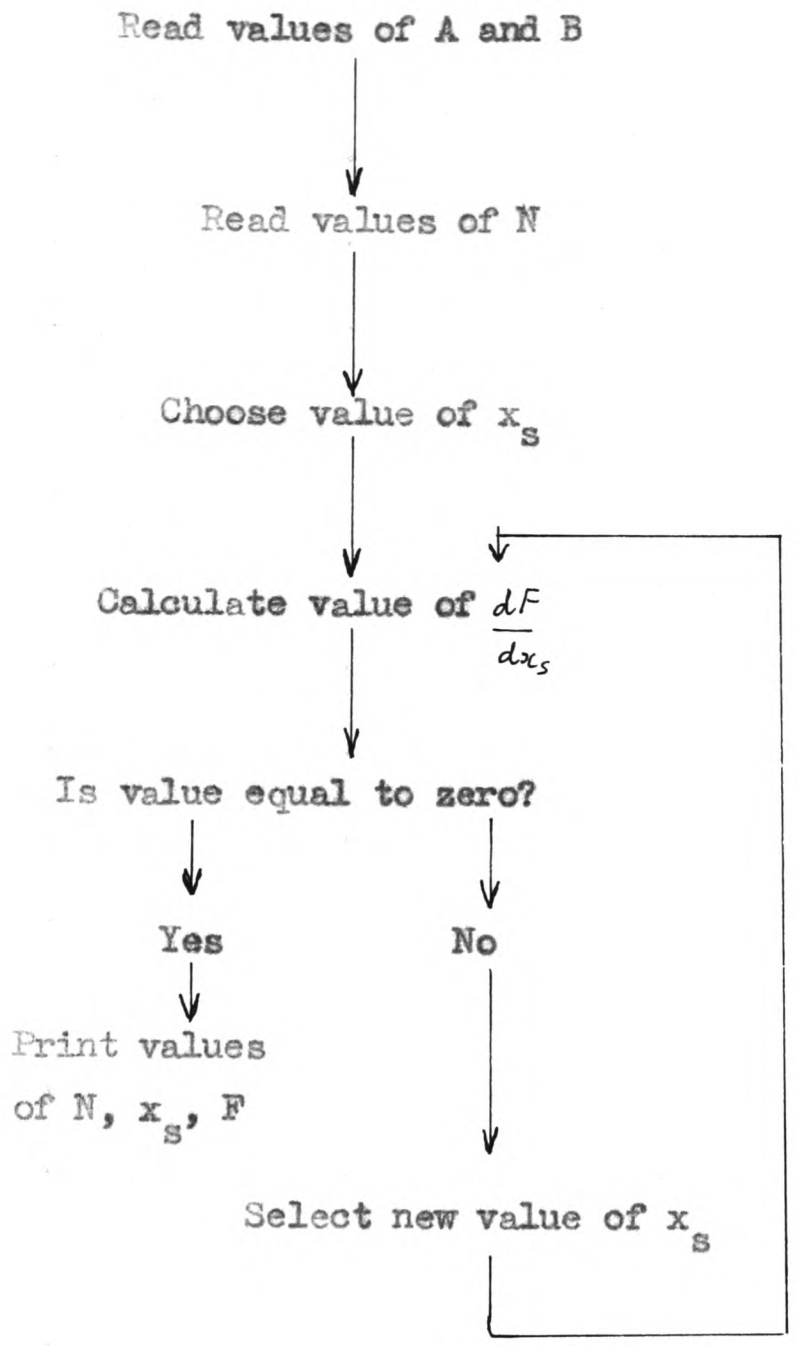
(a = 1.049)

N	x_D	x_s	$\frac{\delta N}{N}$
10	0.518	0.388	3.51
12	0.529	0.376	2.98
14	0.541	0.365	2.55
16	0.553	0.354	2.24
18	0.564	0.343	2.02
20	0.576	0.332	1.84
22	0.588	0.321	1.68
24	0.599	0.311	1.58
26	0.610	0.301	1.46
28	0.622	0.291	1.36
30	0.633	0.281	1.31
32	0.644	0.272	1.26
34	0.654	0.262	1.21
36	0.665	0.253	1.15
38	0.676	0.244	1.10
40	0.686	0.235	1.06
44	0.706	0.218	1.04
48	0.725	0.202	1.01
52	0.744	0.187	0.98
56	0.763	0.174	0.95
60	0.778	0.159	0.92

The percentage error ($\delta N/N$) is computed from values of $\delta p = 0.75 \times 10^{-4}$, A = 7.2, B = - 43.2; as with the values in Table III, A and B are calculated from the functional relationship given by Willingham et al:

$$n_D^{25} = 1.38901 = 0.0244\ x' + 0.0072\ (x')^2$$

Block diagram of computer programme



Appendix C

Experimental results from Column I.

Section I

Results from Column I using n-heptane-methylcyclohexane test mixture. Column length l = 61 cm. Annular gap b = 0.3 cm. $b/r_o = 0.230$

All refractive index measurements were made by means of an Abbe refractometer at 25°C. Values of mole fraction were calculated from the expressions given by Willingham et al (43):

$$n_D^{25} - 1.3851 = 0.0306\ x' + 0.0048\ (x')^2$$

where x' is the mole fraction of methylcyclohexane, n_D^{25} is the refractive index of the mixture.

Values of N, number of theoretical plates, were then calculated from the Fenske equation assuming constant $\alpha = 1.075$. A short computer programme was written to perform these calculations. In Table I the upper values of refractive index and mole fraction refer to the stillpot samples, the lower to the distillate samples.

Values of boilup rate were measured using the boilup meter, except those marked with an asterisk which were estimated from the heat input to the stillpot.

Rotor speeds were measured with a stroboscope.

n_D^{25} - refractive index

x - mole fraction more volatile component

N - no. of theoretical plates per column length (l=6 cm)

n - rotor speed in rpm.

Q - boilup rate in ml./hr.

Table I

Run No.	n_D^{25}	x	N	n (rpm)	Q (ml/hr)	Remarks
1	1.4169	0.09				During
	1.4062	0.38	31.4	2650	560	these runs
2	1.4138	0.17				(1 - 23)
	1.3972	0.62	27.7	2650	560	no
3	1.4121	0.21				thermistor
	1.3961	0.66	26.5	2250	560	balance
4	1.4158	0.12				could be
	1.4007	0.53	28.1	2250	520	achieved.
5	1.4088	0.30				Wall temps.
	1.3949	0.69	21.9	2250	540	high.
6	1.4140	0.17				Evidence of
	1.4009	0.52	22.5	2200	595	leaking
7	1.4090	0.30				ground glass
	1.3992	0.57	14.8	2200	620	joints
8	1.4091	0.29				
	1.3973	0.62	18.1	2200	630	
9	1.4102	0.27				
	1.3990	0.57	17.3	2200	625	
10	1.4106	0.25				
	1.4029	0.46	11.9	650	610	
11	1.4112	0.24				
	1.3997	0.55	18.1	650	620	
12	1.4122	0.21				
	1.4022	0.51	17.8	650	625	

Run No.	n_D^{25}	x	N	n	Q	Remarks
13	1.4130	0.19				
	1.4011	0.51	19.8	650	625	
14	1.4159	0.12				
	1.4062	0.37	19.9	650	605	
15	1.4088	0.30				
	1.4031	0.46	8.3	0	610	
16	1.4100	0.27				
	1.4010	0.52	13.7	300	600	
17	1.4111	0.24				
	1.4013	0.51	15.4	0	600*	
18	1.4122	0.21				
	1.4032	0.46	14.7	0	555	
19	1.4138	0.17				
	1.4027	0.47	19.2	300	535	
20	1.4138	0.17				
	1.4072	0.35	12.1	0	615	
21	1.4131	0.19				
	1.4063	0.37	11.8	0	615	
22	1.4111	0.24				
	1.4009	0.52	16.0	300	650	
23	1.4024	0.48				
	1.3900	0.84	23.6	300	640	
24	1.4166	0.10				Adiabatic
	1.3941	0.72	42.6	2000	480	conditions
25	1.4170	0.09				realised
	1.3982	0.60	36.8	2000	480	for runs
26	1.4142	0.16				(24 - 44)
	1.3931	0.75	37.0	2000	480	

Run No.	n_D^{25}	x	N	n	Q	Remarks
27	1.4140	0.17				
	1.4012	0.51	22.1	0	475	
28	1.4140	0.17				
	1.4050	0.41	16.1	0	480*	
29	1.4142	0.16				
	1.3984	0.59	27.1	0	480*	
30	1.4140	0.17				
	1.4050	0.41	16.1	0	480	
31	1.4150	0.14				
	1.4020	0.49	23.6	520	485	
32	1.4134	0.18				
	1.3958	0.67	29.6	520	480	
33	1.4130	0.19				
	1.4052	0.40	13.3	0	480*	
34	1.4139	0.17				
	1.4072	0.35	12.3	520	480*	
35	1.4120	0.22				
	1.4011	0.51	17.5	0	480*	
36	1.4127	0.20				
	1.3998	0.55	21.1	0	480*	
37	1.4127	0.20				Column pre-
	1.4020	0.49	17.7	0	465	flooded for
38	1.4132	0.19				all sub-
	1.4017	0.50	19.3	0	460*	sequent
39	1.4138	0.17				runs at
	1.4012	0.51	21.5	520	475	zero and
40	1.4141	0.16				low rotor
	1.4049	0.41	16.5	0	470	speeds.

Run No.	n_D^{25}	x	N	n	Q	Remarks
41	1.4143	0.16				
	1.4060	0.38	15.3	0	470*	
42	1.4119	0.22				
	1.3991	0.57	20.5	0	470*	
43	1.4128	0.20				
	1.3993	0.57	22.2	0	470*	
44	1.4131	0.19				
	1.4052	0.40	13.6	0	470*	

Section II

Results from Column I using 2,2,4 trimethylpentane-methylcyclohexane test mixture. Column dimensions as in Section I.

Refractive index measurements were made by means of a drum-reading Abbé refractometer using sodium illumination at 25°C. Values of mole fraction were calculated from an expression given by Willingham et al (43):

$$n_D^{25} - 1.38901 = 0.0244\ x' + 0.0072\ (x')^2$$

where x' is the mole fraction of methylcyclohexane.

As before, values of N were calculated by means of a computer programme. Relative volatility $\alpha = 1.049$.

The independent variables were measured as before.

Symbols have the meanings assigned in Table I.

Table II

Run No.	n_D^{25}	x	N	n	Q	Remarks
45	1.41249	0.220				
	1.40656	0.390	16.4	0	495	
46	1.41438	0.165				
	1.41161	0.245	9.0	0	680	
47	1.41269	0.215				
	1.40235	0.520	28.1	2000	495	
48	1.41336	0.195				
	1.40177	0.540	324	2000	350	
49	1.41336	0.195				
	1.40665	0.390	19.2	2000	820	
50	1.41365	0.185				
	1.40512	0.435	24.4	2000	655	
51	1.41440	0.165				
	1.40928	0.310	16.1	2000	240	
52	1.41522	0.145				
	1.40722	0.370	25.4	2000	600	
53	1.41295	0.205				
	1.40695	0.380	16.9	1600	800	
54	1.41357	0.190				
	1.40548	0.425	23.1	1600	645	
55	1.41190	0.240				
	1.40190	0.535	26.7	1600	525	
56	1.41269	0.255				
	1.40333	0.490	24.1	1600	365	
57	1.41428	0.170				Overheating
	1.40725	0.370	21.2	670	600	of reflux

Run No.	n_D^{25}	x	N	n	Q	Remarks
58	1.41453	0.160				occurred in
	1.40765	0.350	20.5	670	500	runs (57 -
59	1.41458	0.160				80)
	1.41109	0.260	11.5	670	780	
60	1.40937	0.305				
	1.40273	0.510	16.7	670	360	
61	1.40955	0.300				
	1.40576	0.415	9.3	0	360*	
62	1.40996	0.290				
	1.40741	0.365	6.1	0	650*	
63	1.41012	0.285				
	1.40452	0.455	14.2	670	535	
64	1.41362	0.190				
	1.40868	0.325	14.0	670	680	
65	1.41369	0.190				
	1.40998	0.290	10.5	670	750	
66	1.41373	0.185				
	1.40666	0.385	20.6	670	455	
67	1.41237	0.220				
	1.40231	0.520	27.1	670	375	
68	1.41204	0.230				
	1.40217	0.525	264	670	370	
69	1.41216	0.225				
	1.40173	0.540	28.0	670	200	
70	1.41287	0.205				
	1.40632	0.400	18.3	670	200	
71	1.41290	0.205				
	1.40873	0.325	11.9	670	670	

Run No.	n_D^{25}	x	N	n	Q	Remarks
72	1.41328	0.195				
	1.40811	0.325	13.4	670	680	
73	1.41386	0.180				
	1.40825	0.340	16.8	670	600	
74	1.40848	0.335				
	1.40153	0.545	17.4	670	540	
75	1.40924	0.310				
	1.40300	0.500	15.7	670	580	
76	1.41345	0.190				
	1.40791	0.350	16.2	2850	520	
77	1.41237	0.220				
	1.40420	0.465	22.2	2850	525	
78	1.41236	0.220				
	1.40625	0.400	16.7	2850	675	
79	1.41284	0.210				
	1.40794	0.350	13.9	2850	790	
80	1.41408	0.175				
	1.40366	0.480	29.9	2850	365	
81	1.41232	0.225				Adiabatic
	1.40325	0.490	24.5	1470	430	conditions
82	1.41296	0.205				for runs
	1.40265	0.510	28.3	1470	620	(81 - 102)
83	1.41320	0.200				
	1.40544	0.425	21.8	1470	750	
84	1.41337	0.195				
	1.40634	0.395	20.1	1470	360	
85	1.41385	0.180				
	1.40452	0.455	26.7	1470	450	

Run No.	n_D^{25}	x	N	n	Q	Remarks
86	1.41336	0.195				
	1.40584	0.410	21.4	1470	755	
87	1.41372	0.185				
	1.40018	0.590	37.9	1470	440	
88	1.41408	0.175				
	1.40406	0.465	27.5	1470	600	
89	1.41541	0.140				
	1.40406	0.465	34.6	1470	260	
90	1.41015	0.285				
	1.39921	0.625	28.8	1470	365	
91	1.41037	0.280				
	1.39901	0.630	30.1	1470	470	
92	1.41216	0.225				
	1.40107	0.560	29.8	1470	535	
93	1.41481	0.155				
	1.40362	0.480	33.0	2850	575	
94	1.41537	0.145				
	1.40394	0.465	34.7	2850	430	
95	1.41637	0.110				
	1.40858	0.330	27.6	2850	740	
96	1.41312	0.200				
	1.40479	0.445	23.2	2850	740	
97	1.41344	0.190				
	1.40483	0.455	24.3	2850	680	
98	1.41380	0.180				
	1.40376	0.475	28.5	2850	435	
99	1.41240	0.220				
	1.40220	0.525	27.5	2850	565	

Run No.	n_D^{25}	x	N	n	Q	Remarks
100	1.41268	0.225				
	1.40123	0.555	30.8	2850	470	
101	1.41388	0.195				
	1.40268	0.510	31.7	670	540	
102	1.41419	0.170				
	1.40381	0.470	29.9	670	605	

Appendix D

Experimental results from Column 2

Results from Column 2 using 2.2.4 trimethylpentane-methylcyclohexane test mixture. Dimensions are:

Column length $l = 125$ cm.

Annular gap $b = 1.25$ cm

$b/r_o = 0.233$

Symbols are those given in Appendix C Section I with the exception of N, which is number of theoretical plates in 125 cm. Refractive index measurements and calculation of N were made as described in Appendix C Section II

Table I

Run No.	n_D^{25}	x	N	n	Q	Remarks
103	1.41653	0.105	7.7	1670	8800	Runs 103-109
	1.41481	0.155				no PTFE
104	1.41396	0.175	9.0	1670	4250	wipers
	1.41112	0.250				attached to
105	1.41396	0.175	10.2	1670	2530	rotor
	1.41075	0.265				
106	1.41428	0.170	11.7	1670	2530	
	1.41063	0.270				
107	1.41437	0.166	12.7	1670	2000	
	1.41091	0.275				
108	1.41437	0.166	11.9	1670	4830	
	1.41067	0.270				
109	1.41316	0.199	8.3	1670	8800	
	1.41019	0.285				
110/						

Run No.	n_D^{25}	x	N	n	Q	Remarks
110	1.41380	0.180				PTFE wipers
	1.40838	0.335	16.2	1670	4250	attached to
111	1.41416	0.170				improve reflux
	1.40930	0.310	15.1	1670	4250	distribution
112	1.41313	0.200				Run 110 on
	1.40654	0.390	18.7	1670	2660	
113	1.41546	0.135				
	1.41145	0.245	14.4	1670	2600	
114	1.41324	0.195				
	1.40890	0.320	12.7	1670	4100	
115	1.41320	0.200				
	1.40882	0.325	12.8	1670	4150	
116	1.41329	0.195				
	1.40939	0.305	11.5	1670	6250	
117	1.41330	0.195				
	1.40875	0.325	13.3	1670	2450	
118	1.41332	0.195				
	1.41023	0.280	9.1	1670	8500	
119	1.41324	0.195				
	1.40878	0.324	13.0	1670	2450	
120	1.41345	0.190				
	1.41000	0.290	10.5	1670	8650	
121	1.41336	0.195				
	1.41055	0.275	8.3	1000	8650	
122	1.41360	0.185				
	1.40918	0.315	13.2	1000	4150	
123	1.41385	0.180				
	1.40779	0.350	17.5	1000	2450	
124/						

Run No.	n_D^{25}	x	N	n	Q	Remarks
124	1.41327	0.195				
	1.41155	0.245	4.9	100	4150	
125	1.41327	0.195				
	1.41203	0.231	3.3	100	6660	
126	1.41412	0.175				
	1.40741	0.365	19.1	100	4150	
127	1.41336	0.195				
	1.41108	0.259	6.8	100	4150	
128	1.41316	0.200				
	1.41192	0.235	3.3	100	6660	Runs 103-129
129	1.41372	0.185				obtained with
	1.41239	0.220	3.8	100	8650	non-adiabatic
130	1.41434	0.170				conditions on
	1.41157	0.244	9.0	1000	7400	column wall
131	1.41434	0.170				Adiabatic
	1.41133	0.251	9.8	1000	7400	operation for
132	1.41442	0.165				Runs 130 on.
	1.41185	0.237	8.4	1000	7400	High heat loss
133	1.41165	0.242				from stillpot
	1.40855	0.332	8.2	1000	7400	for Runs 103-
134	1.41157	0.244				134(2400Ml/hr)
	1.40815	0.343	9.0	1000	6160	Reduced(400
135	1.41161	0.243				ml/hr) for all
	1.40883	0.323	7.3	850	8000	runs 135 on
136	1.41165	0.242				
	1.40823	0.341	9.1	850	6040	
137	1.41169	0.241				
	1.40711	0.374	12.2	850	4340	

138/

Run No.	n_D^{25}	x	N	n	Q	Remarks
138	1.41169	0.241				
	1.40570	0.416	16.0	850	2520	
139	1.41173	0.240				
	1.40908	0.319	7.2	850	8000	
140	1.41177	0.238				
	1.40851	0.332	8.7	850	6040	
141	1.41177	0.238				
	1.40727	0.369	12.1	850	4000	
142	1.41177	0.238				
	1.40582	0.413	15.9	850	2520	
143	1.41173	0.240				
	1.40695	0.379	12.8	850	4000	
144	1.41173	0.240				
	1.40799	0.348	10.0	1275	6040	
145	1.41185	0.236				
	1.40702	0.377	13.0	1275	4000	
146	1.41189	0.235				
	1.40710	0.374	12.9	1275	4000	
147	1.41189	0.235				
	1.40590	0.410	16.1	1275	2520	
148	1.41193	0.234				
	1.40831	0.338	9.8	1275	6040	
149	1.41197	0.233				
	1.40870	0.324	8.6	1275	8000	
150	1.41201	0.232				
	1.40646	0.393	15.0	1275	2520	
151	1.41209	0.229				
	1.40726	0.369	13.2	1900	4000	
152/						

Run No.	n_D^{25}	x	N	n	Q	Remarks
152	1.41221	0.226				
	1.40835	0.337	10.6	1900	6040	
153	1.41229	0.224				
	1.40863	0.329	10.1	1900	8000	
154	1.41233	0.234				
	1.40904	0.317	9.3	1275	8000	
155	1.41225	0.226				
	1.40980	0.321	9.1	1900	10000	
156	1.41233	0.223				
	1.40879	0.324	9.8	1900	2520	
157	1.41237	0.221				
	1.40679	0.385	15.5	850	2520	
158	1.41241	0.221				
	1.41016	0.284	6.1	850	10000	
159	1.41225	0.225				
	1.40782	0.353	12.2	1900	2520	
160	1.41227	0.224				Runs 160-179
	1.40614	0.403	16.7	1275	4000	with sweeping
161	1.41229	0.224				wires stirring
	1.40658	0.390	15.6	1275	2520	reflux film.
162	1.41232	0.223				
	1.40473	0.446	20.6	1275	6040	
163	1.41229	0.224				
	1.40553	0.422	18.4	1275	8000	
164	1.41236	0.222				
	1.40625	0.400	16.7	1275	10000	
165	1.41249	0.218				
	1.40726	0.369	14.5	1275	14000	

166/

Run No.	n_D^{25}	x	N	n	Q	Remarks
166	1.41257	0.216				
	1.40436	0.458	22.4	1275	4000	
167	1.41257	0.216				
	1.40554	0.421	19.3	1275	8000	
168	1.41259	0.215				
	1.40720	0.371	15.0	1275	14000	
169	1.41261	0.215				
	1.40690	0.380	15.9	1275	12000	
170	1.41271	0.211				
	1.40920	0.310	9.7	850	14000	
171	1.41273	0.211				
	1.40775	0.355	14.0	850	8000	
172	1.41273	0.211				
	1.40706	0.375	15.9	850	6040	
173	1.41277	0.210				
	1.40847	0.334	12.2	850	10000	
174	1.41281	0.209				
	1.40791	0.350	13.9	850	8000	
175	1.41305	0.202				
	1.40932	0.309	10.8	850	12000	
176	1.41325	0.197				
	1.40646	0.393	19.3	1900	14000	
177	1.41349	0.190				
	1.40541	0.425	23.0	1900	8000	
178	1.41366	0.186				
	1.40541	0.425	23.6	1900	6000	
179	1.41386	0.180				
	1.40654	0.391	21.4	1900	10000	
180/						

Run No.	n_D^{25}	x	N	n	Q	Remarks
180	1.41213	0.228				Runs 180-186
	1.40944	0.305	7.3	850	10000	with sweeping
181	1.41217	0.227				wires
	1.40863	0.329	9.7	850	6000	tightened to
182	1.41217	0.227				stir vapour
	1.40827	0.339	10.7	1275	6000	only
183	1.41221	0.226				
	1.40896	0.319	8.9	1275	8000	
184	1.41225	0.225				
	1.40819	0.342	11.2	1275	6000	
185	1.41410	0.173				
	1.41101	0.260	9.8	1900	10000	
186	1.41406	0.174				
	1.41049	0.275	11.2	1900	6000	

Notation

Symbol	Description	Units
A	Constant defined in text	
B	second virial coefficient	cc/mole
b	gap width	cm
C_{12}	Sutherland constant	
D	diffusivity	cm^2/sec
d	diameter	cm
g	acceleration due to gravity	cm/sec^2
H	height equivalent to theoretical plates	cm
H^E	heat of mixing	cal/mole
h	heat transfer coefficient	cm/sec
k	mass transfer coefficient	cm/sec
l	column length	cm
M	molecular weight	g
N	number of theoretical plates	
n	rotor speed	rev/min
n_D^{25}	refractive index at 25°C	
$P_{1,2}$	vapour pressure of components 1,2	$dynes/cm^2$
P_c	critical pressure	atmosphere
Q	boilup rate	ml/hr
R	gas constant	cal/mole/°K
r	radius	cm
	distance in Lennard Jones equation	
s	slope of graph defined in text	
T	temperature	°K
$\bar{u}$	mean velocity	cm/sec
u	velocity	cm/sec
v/		

$\mathbf{v}$	vapour molal flow rate	moles/sec/cm
V	solute molal volumn	cc/mole
V_c	critical volume	cc
W	width of (vapour or liquid) flow path	cm
X	constant defined in text	
x	liquid mole fraction	
y	vapour mole fraction	
z	gas correction factor	
α	relative volatility	
Γ	constant in text; wetting rate	$cm^3/sec/cm$
γ	activity coefficient; surface tension (dyne/cm)	
δ	proportion of reflux streams	
	kinematic surface tension	γ/ρ
ϵ	Lennard-Jones force constant	
η	dynamic viscosity	poise (unless otherwise stated)
κ	thermal conductivity	$cal/cm/^oK$
λ	wavelength	cm
ν	kinematic viscosity	cm^2/sec
π	total pressure	$dyne/cm^2$
	3.14159 ...	
ρ	density	g/cm^3
σ	Lennard-Jones force constant	
τ	shear stress	$dyne/cm^2$
Ω_D	collision integral	
ω	angular rotational speed	cm^{-1}

Subscripts/

Subscripts.

b	boiling (point)
c	critical
lam.	laminar value of
exp.	experimental value
L,V	refer to liquid and vapour respectively
D,S	refer to distillate and stillpot (mole fractions) respectively
1,2	refer to components 1 and 2 respectively
1,O	in r_1 and r_o to inner and outer radii
II	in H_{II} to H.E.T.P. for both walls equally wetted

Dimensionless groups

$Nu = \frac{hd}{K}$ Nusselt number

$Pr = \frac{c_p \eta}{K}$ Prandtl number

$Re_V = Re = Re_{ax} = \frac{2 \bar{u}_V b}{V}$ Axial vapour phase Reynolds number

$Re_L = \frac{4\Gamma}{\nu_L}$ Liquid phase Reynolds number

$Sc = \frac{\nu}{D}$ Schmidt number

$Sh = \frac{kd}{D}$ Sherwood number

$Ta = \frac{\omega r_1 b}{\nu} \left(\frac{b}{r_o}\right)^{0.5}$ Taylor number

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